THE JOURNAL

OF THE

AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLIX SEPTEMBER 1954 No. 9

CONTENTS:

An Electrographic Study of Chromium Sulfate Complex Ions *By* S. G. SHUTTLEWORTH - - - 598

Para-Nitrophenol as a Fungicide for Leather *By* R. M. LOLLAR - - - - - - - - - - - 605

An Insole Leather Tester *By* I. D. CLARKE and R. M. FLAHARTY - - - - - - - - - - - 624

Alum Retannage of Vegetable-Tanned Insoles Improves Their Serviceability *By* G. W. BEEBE, W. F. HAPPICH, W. S. KIP and J. S. ROGERS. - - - - - - 630

Abstracts - - - - - - - - - - - - - 639

SUBSCRIPTION: Members $12.00 a Year Non-Members $15.00

Published Monthly by

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLICATION OFFICE, EASTON, PA.

Entered as Second-Class Matter at Post Office, Easton, Pa.
Acceptance for Mailing at Special Rate of Postage as Provided for in Section 1103.
Act of October 3, 1917, Authorized July 16, 1918

COPYRIGHT, 1954, THE AMERICAN LEATHER CHEMISTS ASSOCIATION

Reliable Direct Sources the World Over

FOR

VEGETABLE TANNING MATERIALS

QUEBRACHO
WATTLE EXTRACT
WATTLE BARK
MANGROVE BARK
MYRABOLAMS & EXTRACT
VALONEA & EXTRACT
DIVI DIVI
CUTCH
SUMAC—LEAF & GROUND
TARA—PODS & POWDER
OAKWOOD EXTRACT, Swedish
LARCHBARK EXTRACT, Swedish

▼

U. S. of A. Sales Agents for "N.C.S." Brand South African Wattle Extract

U. S. of A. Sales Agents for "SENS" Brand Powdered Valonea Extract

The Olson Sales Agency

Import · Export

20 BROAD STREET (NEAR WALL STREET) NEW YORK 5, N. Y.

Cable Address:
"COROSAGE"

Telephones:
DIGBY 4-0226
0227

I

It Takes Quality To Make Quality!

Socony-Vacuum products have helped make good leather since 1866

Take choice hides . . . add skilled craftsmen . . . and specify Gargoyle tanning products. That's one formula for making *good* leather, proved over nearly a century!

The complete line of Gargoyle tanning products includes Sulfolines . . . Curriers Greases . . . the Solenes, Sole Waterproofing Compounds and micro-crystalline waxes — all made under the most exacting manufacturing standards.

Why not call your Gargoyle representative today?

SOCONY-VACUUM

Gargoyle *Leather Oils & Greases*

SOCONY-VACUUM OIL COMPANY, INC., TANNERS DIVISION, 26 BROADWAY, NEW YORK 4, N. Y.

SPRUCE EXTRACT

POWDERED SUPER SPRUCE

LACTANX

■

Robeson Process Company

General Offices: 500 Fifth Avenue, New York, N. Y.

Operating Plant at Erie, Pa.

MECO EXTRACT

ONE GRADE—THE BEST

CHESTNUT WOOD EXTRACT

All Concentrations, Liquid to Dry Powder

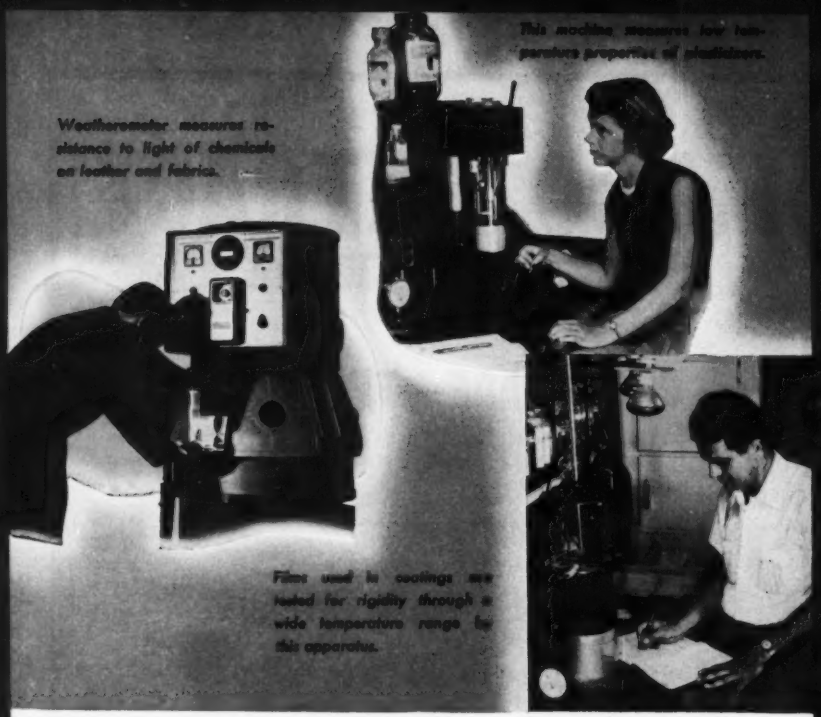
Teas Extract Co.

6400 Centennial Boulevard

NASHVILLE 9, TENNESSEE

TENNESSEE PLANT
Nashville, Tenn.

ANDREWS PLANT
Andrews, N. C


Weatherometer measures resistance to light of chemicals on leather and fabrics.
This machine measures low temperature properties of plasticizers.
Films used in coatings are tested for rigidity through a wide temperature range by this apparatus.

THE SEARCH THAT NEVER ENDS

Once in awhile the question is asked: "What has been the effect on Rohm & Haas leather chemicals of the spread of the company's interest into other fields?" The answer is simple: Chemicals which might not otherwise have been made are now available to the tanner. This has resulted in the development of products of highest quality whose range of usefulness to the tanner is steadily being extended.

Important as our leather business is, it could not by itself support the fundamental research in various fields which has resulted in the development of new and improved leather chemicals for the tanner.

A case in point is ZIRCOTAN, the zirconium tanning agent for producing through-white leather. Initially our interest in zirconium compounds centered around their use as opacifiers for porcelain enamel. Subsequent work on the chemistry of zirconium led to the development of ZIRCOTAN.

Another example is our PRIMAL acrylic leather finishes. This company is the pioneer in acrylics. Knowledge of the toughness and permanent flexibility of acrylic polymers made possible the development of PRIMAL emulsions.

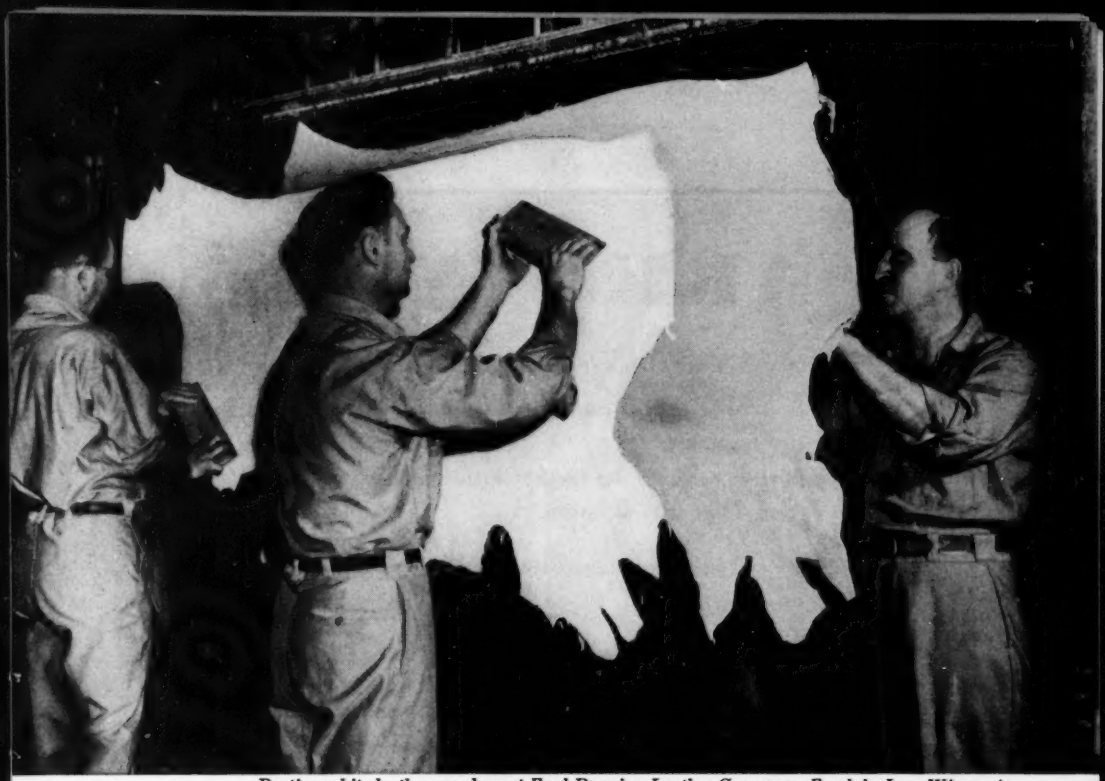
ZIRCOTAN and PRIMAL are trademarks, Reg. U.S. Pat. Off. and in principal foreign countries.

CHEMICALS FOR INDUSTRY

ROHM & HAAS COMPANY

WASHINGTON SQUARE, PHILADELPHIA 5, PA.

Representatives in principal foreign countries



Pasting white leather on glass at Fred Rueping Leather Company, Fond du Lac, Wisconsin.

How TANAK® MRX lets you stretch leather—and still keep it plump!

Pasting wet leather on glass or porcelain plates to dry will give a tanner more footage—but the leather tends to be flat. The addition of TANAK MRX to his white formula allows the tanner to increase his footage yield, tighten the break and still maintain plumpness.

Working with Cyanamid's Technical Staff, many tanners have found they can up-grade their colored leathers, too, decreasing flankiness and tightening break without a reduction in weight by adding or substituting MRX in their re-tan formulations.

Such results have led to wide acceptance of TANAK MRX in the production of white, colored and natural back leathers.

With chemicals for virtually every tanning process, and a modern application laboratory, Cyanamid can give you complete service.

To make leather better through chemistry...

Cyanamid recently opened a completely modern application laboratory at Chicago. Perhaps our research program should include *your* tanning problem. Drop us a line.

AMERICAN Cyanamid COMPANY

LEATHER CHEMICALS DEPARTMENT

30 Rockefeller Plaza, New York 20, N. Y.

In Canada: North American Cyanamid Limited, Toronto and Montreal

ARKOTAN®

Highly efficient tanning assist adaptable for vegetable, chrome, alum and formaldehyde tannages.

- Imparts silky grain to the leather with increased roundness and improved tensile strength.
- Can be used as a mordant with excellent results on calf, side and glove leather.
- A perfect pre-tannage for shearlings.
- Produces a clean, white leather when used in conjunction with chrome in the tannage and as a bleach on top.

Information, samples and demonstration upon request.

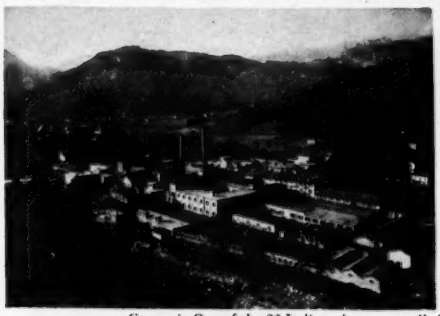
ARKANSAS COMPANY, Inc.
Newark, N. J.

Manufacturers of Industrial Chemicals
for over 50 years

LEDOGA S.p.A.

FOUNDED 1860

LEDOGA



Garressio-One of the 22 Italian plants controlled by Ledoga S.p.A.

WORLD'S LARGEST PRODUCERS OF

CHESTNUT EXTRACTS

Produced in *Italy*

Types: • Regular spray-dried powdered Chestnut Extracts • "Dulcotan", a sweetened Chestnut Extract as a Quebracho substitute

Properties: Highly Concentrated • Double Decolorized • Very Light Colored • Great Purity (due to very low non-tannin contents)

LEDOGA S.p.A. sells the total production of 22 of the 38 plants in Italy making Chestnut Extract.

*

Barkey

Importing Co., Inc.

44 East 53rd Street, New York 22, N. Y.

Exclusive Representative in the United States and Canada

igenal
for full
penetration
on casual
leathers
browns

Specifically created to impart uniform interior coloring and full elk character. Today's casual leathers require Igenal Browns to provide a broad range of browns and tans of unexcelled color performance when combined with surface dyeing direct and acid dyes to produce present day high-fashion color styling.

IGENAL BROWNS PRMA and PGMA assure–

- Uniform penetration
- Slow exhaustion
- Very level dyeing properties on chrome and alum tanned leathers
- Compatibility with all surface dyeing acid and direct dyes

Technical service on your leather coloring problems will always receive our prompt and efficient attention and we invite your valued inquiries.

From Research to Reality

gdc gaf

GENERAL DYESTUFF COMPANY

A SALES DIVISION OF GENERAL ANILINE & FILM CORPORATION

435 HUDSON STREET • NEW YORK 14, NEW YORK

BOSTON • CHARLOTTE • CHATTANOOGA • CHICAGO • NEW YORK • PHILADELPHIA • PORTLAND, ORE. • PROVIDENCE • SAN FRANCISCO

JACQUES WOLF CHEMICALS Produce High Grade Leather

SYNEKTAN 0-230
A liquid synthetic tannage that equals the qualities of vegetable extracts. Replaces Sumac. Used as a retan on chrome stock.

SYNEKTAN NPP
For high grade whites and pastel colors; produces full plump leather.

SYNEKTAN NCRP
Specialty syntan, used in combination with chrome tannage or in the dye bath for better grain.

TANASOL NCO
Syntan in beads, to use with extracts in the tanning and retanning operations.

TANASOL PW
Syntan in beads, to use with NCO for bleaching chrome stock and in retanning chrome stock. In the dye bath for good level colors.

FUNGIZYME BATES
Pancreatic bating salts of standard, controlled quality.

BATE A & AS For sheep skins and sole leather.

BATE B & BS For furniture leather, side leather and calf skins.

BATE C & CS For goat skins.

SULPHONATED OILS (Various Bases)

MONOPOLE OIL (For Finishing)

EMULSIFIERS AND DETERGENTS (For Good Degreasing)

Samples and information upon request.

JACQUES WOLF & CO.
Chemicals PASSAIC, N.J.

Plants in: Clifton, N.J., Carlstadt, N.J., Los Angeles, Calif.

Gives You High Neutralizing Action with Low pH

for UNIFORM QUALITY!

IMPROVED GRAIN!

UPGRADED LEATHERS!

SOLVAY

Other Solvay Products for Tanners

- **CLEANSING SODA XX**
- **SNOWFLAKE* CRYSTALS**

*REG. U. S. PAT. OFF

Soda Ash · Caustic Soda
Potassium Carbonate
Calcium Chloride · Chlorine
Caustic Potash · Sodium Nitrite
Cleaning Compounds
Ammonium Bicarbonate
Sodium Bicarbonate
Snowflake® Crystals
Ammonium Chloride
Monochlorobenzene
Para-dichlorobenzene
Ortho-dichlorobenzene

Get a Finer Finish . . . more uniform dyeing . . . and better quality leathers with SOLVAY Ammonium Bicarbonate.

Superior Leathers are obtained with SOLVAY Ammonium Bicarbonate—because it penetrates the leather uniformly throughout the thickness of the hide—the inner area as well as the surface. SOLVAY Ammonium Bicarbonate has a *high neutralizing* value (greater than borax or sodium bicarbonate) with a *low* pH. A 1% solution has a pH of only 7.8!

Test Samples of SOLVAY Ammonium Bicarbonate are available. Prove to yourself how it gives you *better-looking* leathers—*economically* and *efficiently*. For further information and samples, write or phone the nearest SOLVAY office.

SOLVAY PROCESS DIVISION

ALLIED CHEMICAL & DYE CORPORATION

61 Broadway, New York 6, N. Y.

BRANCH SALES OFFICES:

Boston · Charlotte · Chicago · Cincinnati · Cleveland · Detroit
Houston · New Orleans · New York · Philadelphia · Pittsburgh
St. Louis · Syracuse

QUEBRACHO EXTRACTS

"SUPREMO"
BRAND
SOLID-ORDINARY

"LUNA"
BRAND
COLD WATER SOLUBLE

INTERNATIONAL PRODUCTS CORPORATION

29 BROADWAY, NEW YORK 6, N. Y.

The Only American Manufacturer of Quebracho In South America

FACTORY AT PUERTO PINASCO, PARAGUAY

MANUFACTURERS:
LIQUID QUEBRACHO EXTRACTS
•
FACTORY:
Staten Island, N. Y.

IMPORTERS:
MYRABOLAMS
WATTLE BARK
DIVI-DIVI
VALONIA
ETC.

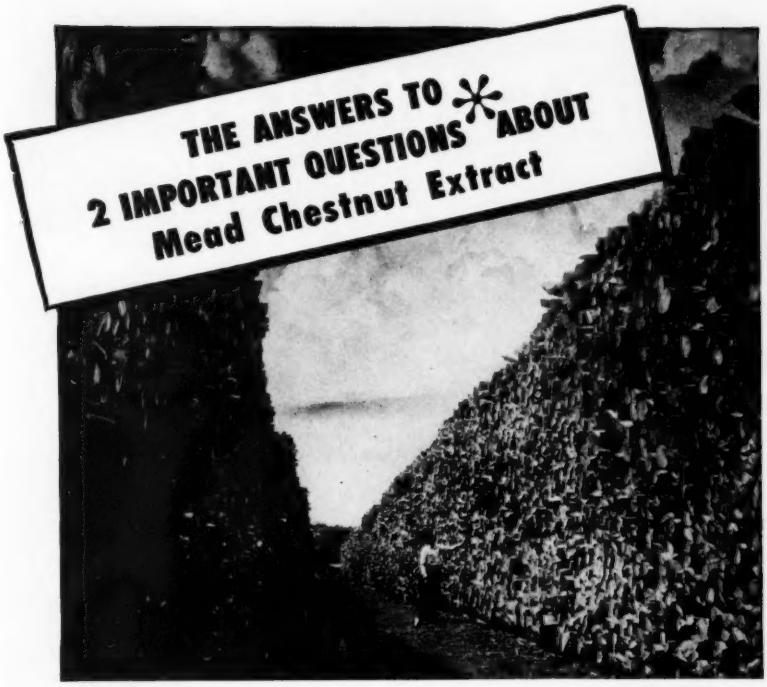
Representatives:

Harvey J. Boutin & Son
San Francisco, Calif.

Yocum Faust, Limited
London, Canada

Gonzalez, Ramirez y Cia
Havana, Cuba

The R. J. Vogel Company
Mexico City, Mexico



This is only a portion of the many stockpiles of chestnut logs that insure a continuous supply of Chestnut Extract.

1. Is the supply of Mead Chestnut Extract adequate?

Decidedly yes. Recent surveys show that there is enough chestnut wood in our forests to serve the leather industry for many years to come. Huge chestnut stockpiles, such as the one shown above, are converted under chemical control at five extract plants, insuring a steady supply of Mead Chestnut Extract.

2. Why is Mead Chestnut Extract preferred over other tanning agents?

Mead Chestnut Extract is a superior tanning material, made by America's largest producer of vegetable tanning extracts. Repeated experience has shown:

A. Chestnut tanned leathers do not oxidize, darken on exposure to light, or develop an uneven color on aging, as do leathers tanned with many other materials, vegetable or synthetic.

B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

Ask about Mead Cold Soluble Chestnut Extract for retanned leathers. And—for more pounds of plumper leather—standardize on Mead Chestnut Extract.

IT'S A FACT!

Mead Chestnut Extract will produce more pounds of plump leather per unit of tannin than any other tanning material.

Vegetable Tannin	Tan Yard Yield (*white weight basis*)
Chestnut Wood Extract	67%
Tanning Material A	61%
Tanning Material B	63%

Calculate your tanning material costs on a leather basis as well as on a tan unit basis. Mead Chestnut Extract, producing four to six pounds more leather, means positive savings.

MEAD
CHESTNUT
EXTRACT

THE MEAD CORPORATION
Tannin Extract Division, Lynchburg, Virginia

THE RIVER PLATE CORPORATION

ORDINARY 'CF dd C' EXTRACT

'CROWN' FORESTAL

Exclusive Agents:

QUEBRACHO

EXTRACTS

WATTLE

ELEPHANT BRAND N.T.E.Co. LTD

MIMOSA KENMOSA EXTRACT

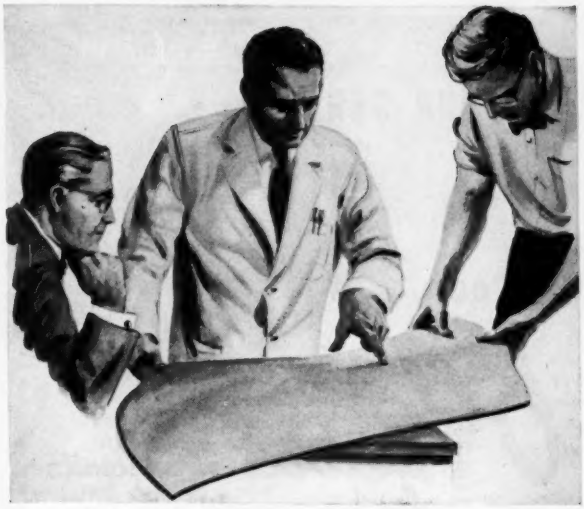
Importers and Processors

Raw Tanning Materials From All Parts of the World

THE RIVER PLATE CORPORATION

CHRYSLER BLDG., NEW YORK 17, N. Y. *Plant:* NEWARK, N. J.

Subsidiary: THE TANNIN CORPORATION of MASS. Office & Plant: Peabody, Mass.



PUT WATTLE INTO YOUR LIQUORS,

you'll get better fixation and color

Today, more than ever, tanners are concerned about the quality of their leather. Good penetration, good color and high degree of tannage are obtained by using wattle extract.

Our extracts, made from the best grades of bark, are pure extracts untreated by any kind of chemical.

WATTLE EXTRACT is suitable for use in the manufacture of all types of leather, ranging from sheepskins for shoe linings to high-grade sole leather.

WATTLE MAKES GOOD LEATHER

SOUTH AFRICAN WATTLE EXTRACT MFRS. ASSO.
Pietermaritzburg, Natal, Union of South Africa
KENYA WATTLE MANUFACTURERS ASSOCIATION
Nairobi, Kenya, East Africa

AT YOUR SERVICE . . .

Let our

64 years *of specialized experience work for you . . . profitably*

ATLAS

Guaranteed **OILS**

- **NEATSFOOT OILS**
- **SULPHONATED COD OILS**
- **SULPHONATED NEATSFOOT OILS**
- **SPLIT OILS**
- **MOELLONS, and many specialty Products**

ATLAS REFINERY SINCE 1867 QUALITY LEATHER OILS NEWARK, N.J.

A Name and Symbol Pre-eminent in the Tannery Industry

● For over half a century, ATLAS has been a leader in the production of Quality Oils for the Tanning Industry, through extensive research to serve you better. ATLAS specialized research, plus many years of practical experience in the production of consistently high-quality, guaranteed oils is your assurance of uniformity to meet definite specifications. Give your leathers the "quality look" with ATLAS Oils.

ATLAS *Refinery, Inc.*

142 LOCKWOOD ST. NEWARK 5, N. J.

Save Hide Substance

USE.. BSM-11 or BUTROL

as part of Good housekeeping practice

BSM-11 is highly effective in controlling the growth of microorganisms which digest hide substance during processing. BSM-11 is a liquid, thus easily added to the systems directly from the drums.

It has been demonstrated in many tanneries that the synergistic combination of bactericides and fungicides in BSM-11 provides efficient, economical control of bacteria, molds and yeasts which damage skins and hides.

Our representative will give technical assistance on the most effective use of BSM-11 in your process.

BUCKMAN
Laboratories, Inc.

Manufacturing Chemists • Memphis 8, Tennessee

Representatives in Most Countries

MICROORGANISM CONTROL SPECIALISTS

What Hooker Sodium Sulfhydrate does for the Leather you make...

SOLE LEATHER—With Hooker Sodium Sulfhydrate, you can increase sulfide strength of the unhairing solution just as desired, and still keep alkalinity low. This means easy unhairing in limited time. Hides are ready when desired—without loss of hide substance from long immersion. *Results:* a minimum of swelling . . . greater yield of tight, solid, smooth-grained leather . . . a significant saving of time and extra operations in the beam-house.

CALFSKINS AND HORSEHIDES—The tender grain of these skins is protected by Hooker Sodium Sulfhydrate from excessive swelling and plumping caused by high alkalinity. With Sodium Sulfhydrate, a minimum of swelling takes place, resulting in a better yield of fine, smooth leather.

GOATSKINS—Destructive bacterial action is held to a minimum, because Hooker Sodium Sulfhydrate increases the solubility of the lime and permits more constant pH value than with Sodium Sulfide. Sulfide content can be built up, with low alkalinity. Alkalinity can be increased or held as desired, without affecting sulfidity. *Result:* Greatly simplified control of quality, even with skins that vary widely in sensitivity.

When dissolved in lime, Hooker Sodium Sulfhydrate forms only half as much caustic soda as the same quantity of Sodium Sulfide forms. This gives you precision control of unhairing solutions—and many other advantages. Write today for a copy of Hooker Bulletin 500, "Sodium Sulfhydrate for the Leather Industry," which suggests unhairing procedures for various leathers.

HOOKER ELECTROCHEMICAL COMPANY

3 UNION ST., NIAGARA FALLS, N. Y.
CHICAGO, ILL. - NEW YORK, N. Y.
LOS ANGELES, CALIF. - TACOMA, WASH.

HOOKER CHEMICALS ®

CHLORINE • SODIUM TETRASULFIDE • SODIUM SULFIDE
CAUSTIC SODA • MURIATIC ACID • PARADICHLOROBENZENE

10-1398

BARKEY

Importing Co. Inc.

44 EAST 53rd STREET • NEW YORK 22, N. Y.

IMPORTERS

VEGETABLE TANNING EXTRACTS AND RAW MATERIALS

- Wattle Bark
- Wattle Extract
- Quebracho Extract
- Mangrove Bark
- Valonia Cups, Beards
- Divi divi
- Valonia Extract, Valex Brand
- Sicily Sumac
- Myrabolans

SOLE AGENTS FOR UNITED STATES & CANADA

for

ITALIAN CHESTNUT EXTRACTS

SOLID & POWDERED

Produced by

LEDOGA S. p. A.

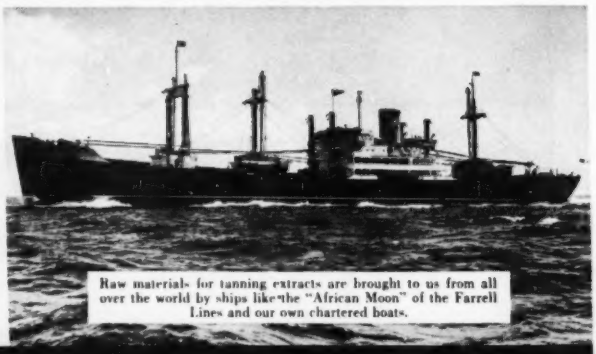
MILANO, ITALY

WATTLE BARK — *from Africa*

SUMAC — *from Sicily*

DIVI-DIVI — *from Santo Domingo*

GAMBIER
— *from Malayan Straits*



Raw materials for tanning extracts are brought to us from all over the world by ships like the "African Moon" of the Farrell Lines and our own chartered boats.

MYRABOLAM — *from India*

The J. S. Young Company

ONE OF AMERICA'S FOREMOST IMPORTERS AND PROCESSORS OF Tanning Extracts

QUERBRACHO
— *from the Argentine*

CHESTNUT WOOD *Extract*
— *from France and Italy*

For three-quarters of a century—since 1879—The J. S. YOUNG CO. continuously has imported, processed and manufactured—in its modern 8½-acre Baltimore plant—highest quality tanning extracts for the industry.

They include:
LOGWOOD • WATTLE BARK • SUMAC • DIVI-DIVI • GAMBIER • QUERBRACHO • MYRABOLAM
OSAGE ORANGE • CHESTNUT WOOD EXTRACT • FUSTIC • HYPERNIC • TANNIC ACID

We are also manufacturers of the famous CHEMBARK natural tanning extracts for the Chemtan Co. and special products for other well-known firms.

The J. S. YOUNG CO.

2701-2733 Boston St., Baltimore 24, Maryland

Experienced technical advice available on request from Baltimore or from any of our branches.

Branches: PHILADELPHIA • CHICAGO • PATERSON, N. J. • DANVERS, MASS.

DEVELOPMENT AND

INTRODUCTION OF

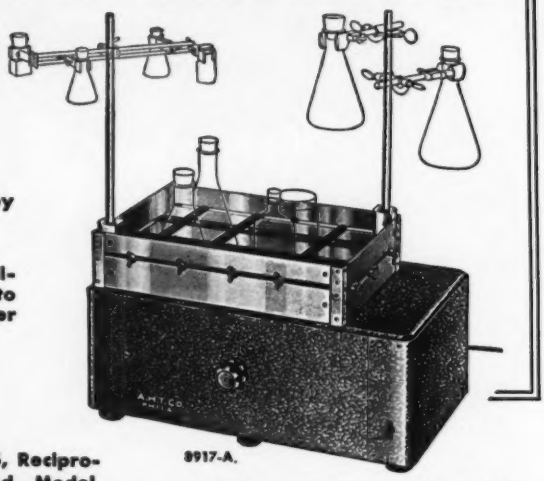
BETTER **CHEM**ICALS FOR **TAN**NING

IMPROVED MODEL, VARIABLE SPEED

SHAKING APPARATUS

RECIPROCATING TYPE

- **For *continuous* operation**
- **Stepless split-pulley speed control**
- **Oscillations variable from 65 to 240 strokes per minute**



8917-A.

SHAKING APPARATUS, Reciprocating Type, Improved Model, Variable Speed. A rugged, relatively quiet Shaker for general purpose use, consisting of a carrier of corrosion-resistant metal and variable speed power unit suitable for *continuous* operation.

Power unit is furnished with constant speed, 1725 r.p.m. synchronous ¼ h.p. motor which operates at full speed and maximum torque, but speed of platform oscillation is variable by means of a special belt-driven, variable pitch pulley system employing a countershaft and two split pulleys, one of which is changed manually by a hand wheel and locking nut operated from the front of the housing. Oscillations can be varied between approximately 65 and 240 strokes, each 1-½ inches long, per minute.

Housing is finished in gray Hammertone enamel, outside dimensions 23-½ inches long x 11-½ inches wide x 9-¾ inches high, and includes six rubber suction-cup feet which anchor the Shaker securely to the table and eliminate the tendency to creep.

The box-type Carrier consists of an anodized aluminum box, 18 inches long x 12 inches wide x 3-¾ inches deep, with rubber-covered floor and slotted sides and ends to take adjustable, rubber-covered bars lengthwise and crosswise for holding various types of load in position. The utility of this carrier is greatly increased by posts which are attached to the corners of the tray. The posts are fitted with ½-inch rods, 18 inches long, with threaded ends, on which a variety of clamps, glassware, etc., can be mounted for shaking.

8917-A. Shaking Apparatus, Variable Speed, General Purpose, as above described, consisting of power unit, aluminum box-type carrier, two clamping bars with washers and wing nuts for attachment to sides, and two corner posts with eight screws for attachment. Power consumption 200 watts. Complete with on-off switch, connecting cord and plug; for use on 115 volts, a.c. . . **223.50**
8917-D. Ditto, but without clamping bars or corner posts **201.50**

QUALITY AND SERVICE
A.H.T.CO.
PHILA. U.S.A.
LABORATORY APPARATUS

ARTHUR H. THOMAS COMPANY

Laboratory Apparatus and Reagents

WEST WASHINGTON SQUARE **PHILADELPHIA 5, PA.**

Teletype Services: Western Union WUX and Bell System PH-72

JOURNAL OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLIX SEPTEMBER 1954 No. 9

DEAN WILLIAMS ..... *Editor*

EDITORIAL BOARD

H. B. MERRILL R. B. HOBBS F. O'FLAHERTY
R. E. PORTER J. H. HIGHBERGER H. G. TURLEY

Only such correspondence as pertains to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Correspondence in reference to subscriptions, advertising and other business should be addressed to the Secretary, Dept. of Leather Research, University of Cincinnati, Cincinnati 21, Ohio.

Checks for subscriptions and advertisements should be made payable to the American Leather Chemists Association.

Subscriptions—Members, $12.00 annually; Non-members, $15.00 annually.

Published monthly by the American Leather Chemists Association.

Entered as Second-class Matter at the Post Office at Easton, Pa.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 16, 1918.

Copyright 1954, by the American Leather Chemists Association.

PAST PRESIDENTS OF THE A. L. C. A.

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VETCH, W. K. ALSOP, L. E. LEVI, C. R. OBERFELL, R. W. GRIFFITH, C. C. SMOOT, III, J. S. ROGERS, LLOYD BALDERSTON, J. A. WILSON, R. W. FREY, G. D. McLAUGHLIN, FRED O'FLAHERTY, A. C. ORTHMANN, H. B. MERRILL, V. J. MLEJNEK, J. H. HIGHBERGER, DEAN WILLIAMS, T. F. OBERLANDER, A. H. WINHEIM, R. M. KOPPENHOEFER, H. G. TURLEY.

OFFICERS 1953-'54

President—E. S. Flinn, Ardslea, Route 8
Chillicothe, Ohio.

President-Elect—E. B. Thorstensen, S. B. Foot Tanning Company, Red Wing, Minnesota.

Secretary-Treasurer—Fred O'Flaherty, Department of Leather Research, University of Cincinnati, Cincinnati, Ohio.

Council

R. G. Henrich, Surpass Leather Company, 9th and Westmoreland Streets, Philadelphia 40, Pennsylvania.

H. R. Wilson, B. D. Eisendrath, Memorial Laboratory, 702 Racine Street, Racine, Wisconsin.

J. R. Kanagy, 9922 Sutherland Road, Silver Spring 5, Maryland.

Mieth Maeser, United Shoe Machinery Corporation, Research Division, Balch Street, Beverly, Massachusetts.

Dominic Meo, Jr., Salem Oil and Grease Company, Salem, Massachusetts.

An Electrographic Study of Chromium Sulfate Complex Ions.

By S. G. SHUTTLEWORTH

Electrophoretic work on the basic chromium sulfate complexes has been carried out by Plant [1], who constructed a simple U-tube form of glass apparatus and passed a current between two platinum electrodes immersed in the solution. He concluded that a freshly boiled 10 g./liter chrome alum solution contained only positively charged complexes, while a freshly boiled 150 g./liter chrome alum solution contained only negatively charged complexes. In view of the evident clash of the latter finding with the analytical data of Atkin and Chollett [2] the writer has tested out Plant's apparatus and has concluded that rapid diffusion of free sulfate ions through the narrow U tube, could give rise to currents which might well reverse the true migration of a slow moving chrome complex ion in a concentrated solution.

An alternative method of estimating the charge on the complex is the use of ion exchangers, but the results obtained by different workers have shown serious disagreement. For example Adams [3] has found that additions of from 1 to 4 moles per mole Cr_2O_3 of sodium sulfate (0.3 moles per liter) to a basic chromium sulfate liquor had little effect on the removal of chromium sulfate by a cationic exchanger regardless of whether the solutions were fresh or aged 24 hours. On the other hand Gustavson [4] found that the addition of 1 mole per liter of sodium sulfate to a one third basic chrome liquor caused a drop in cationic complexes from 96 per cent to 55 per cent. Analytical and spectrophotometric results obtained by the writer [5] are also at variance with Gustavson's results. On the other hand the cationic complexes removed by Adams were found to be about 70 per cent basic as compared with the 40 per cent basicity of the starting liquor, whereas Gustavson's complexes were very little modified in basicity by the exchange resin treatment. The differences between the results of Adams [3] and Gustavson [4], may be partly explained by the lower concentrations used by Adams, which would give greater hydrolysis and lower sulfate co-ordination. The success of the exchange resin technique depends on the absence of any affinity between chromium complex and resin apart from the electrostatic attraction between oppositely charged ions. It is probable that secondary effects are present, particularly where highly olated chromium complexes are being examined. Furthermore, very large particles may appear as non cationic by failing to penetrate the cationic resin.

The combination of paper chromatography and electrophoretic techniques offers a method of determining not only the charge on the complex but also the homogeneity of the solution.

Apparatus Used

This was developed by Cooper [6] from a description by Kunkel and Tiselius [7], and consisted essentially of high voltage direct current supplied to two shal-

low dishes 6″ x 10″ containing 0.05*N* nitric acid connected electrically by a sheet of Asoka white blotting paper No. 38. The paper passed between two greased glass plates 8″ x 10″ in area, clamped firmly between teak boards of slightly larger area. Before use, the paper was soaked in 0.05*N* nitric acid, surface liquid blotted off, and spotted with the chromium complexes down a center line marked in advance on the dry paper. Spots were of ½ to ⅔ inches in diameter and were centered exactly on the line. A potential of 250 volts applied across the paper for 1 hour was found to give good results, the operating current being about 60 milliamps. It should be noted that Tiselius[7] used an operating current of 20 milliamps on a 2-inch wide paper strip. The use of 60 milliamps on an 8-inch wide strip gives less heating of the plates. After each run the plates were tested for heating and found to have not risen appreciably in temperature.

The use of 0.05*N* nitric acid as electrolyte prevents diffusion of acid away from the complex, which would result in hydrolysis followed by olation. Work to be published will show that olation is far more rapid than deolation, so that there is less danger of complex change on dilution when H ions are present. A check showed that penetration of H ions into the complex after 1 hour under the above conditions was negligible.

Results

(a) *Chrome Alum*:

The 10 g. per liter concentration was too dilute to give a satisfactory spot on the electrogram, but as there appears to be no doubt about the positively charged nature of the complexes at this concentration, the matter was not pursued further.

FIG. 1. CHROME ALUM.

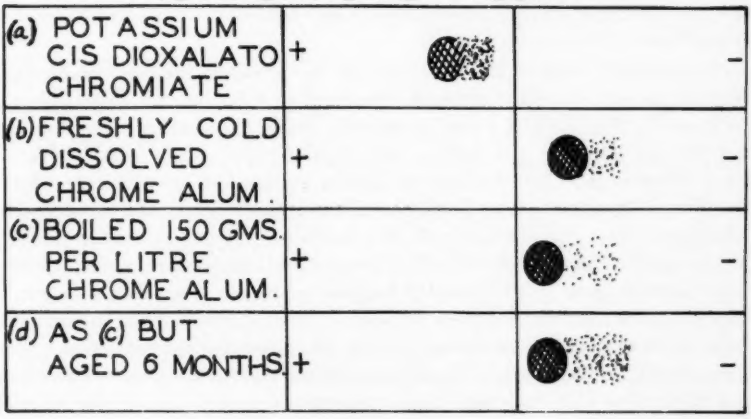


Fig. 1 shows the electrograms recorded in a simultaneous run of pure *cis* potassium dioxalato chromiate, 150 g. per liter chrome alum freshly boiled and aged 6 months, and freshly dissolved violet chrome alum (not heated).

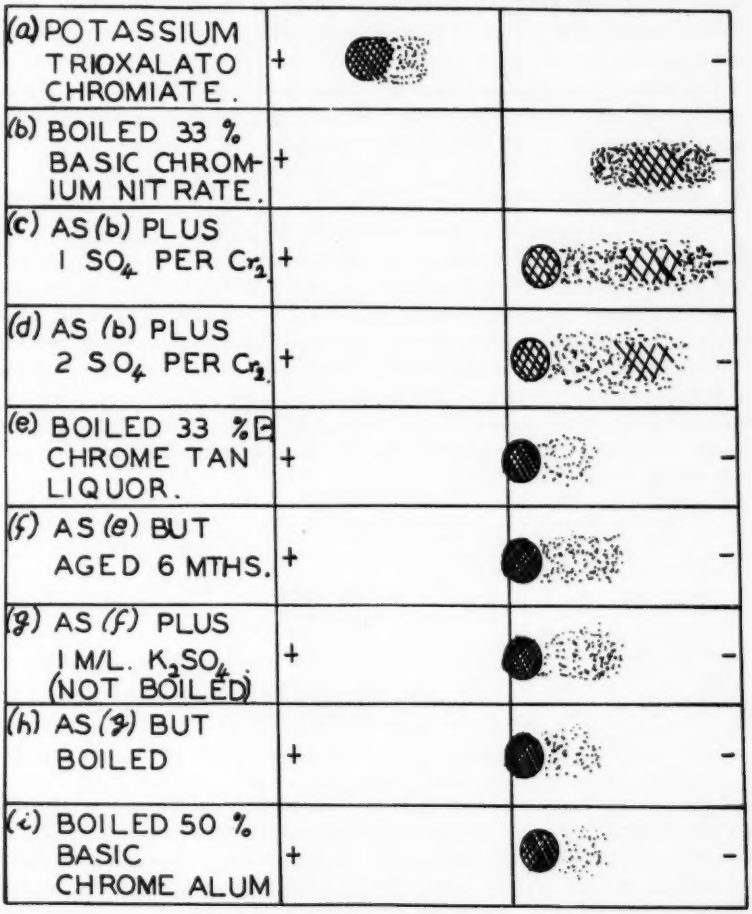
It is apparent that the dioxalato chromiate (Fig. 1a) which has one negative charge, has moved appreciably faster than the triple-charged violet chrome alum ion (Fig. 1b), indicating that the latter has a low mobility. The violet chrome alum ion gave a well defined single spot, with a very faint forward trail. The reason for this faster moving trail is not apparent. The boiled and aged chrome alums (Fig. 1c and 1d.) were very similar, both giving well defined spots with faint forward trails but the aged complex showed more trail than the freshly boiled complex. The complexes were all positively charged, showing that Plant's electrophoretic experiments [1] have led him to erroneous conclusions. The rate of movement and the shape of the spots indicate that most of the chromium in the 150 g. per liter boiled chrome alum is in the form of a single complex of low mobility carrying a positive charge. The trails are evidently due to dissociation of sulfate ions from the complex, giving two extra positive charges for each sulfate dissociated, with consequent increased rate of migration in the charged field. These results fit the analytical data of Atkin and Chollet [2].

(b) *Basic Chromium Sulfates*:

Fig. 2 shows the electrograms recorded in two runs under identical conditions with pure potassium trioxalato chromiate as standard. It is apparent that the olated chromium complexes formed in the absence of sulfate ions are fairly mobile and/or highly charged. An olated dimer would carry four positive chrages, while a four-chrome molecule would carry eight charges. A comparison with the shape of the trioxalato complex (Fig. 2a) suggests that the freshly boiled 33 per cent basic chromium nitrate solution (Fig. 2b) contains mainly an olated dimer plus a lesser proportion of larger complexes (responsible for the forward trail).

The stepwise addition of sulfate ions to this complex followed by boiling, results in mixed positively charged complexes at 1 SO_4 per Cr_2 (Fig. 2c) and 2 SO_4 per Cr_2 (Fig. 2d) but a single positively charged spot of very low mobility at 4 SO_4 per Cr_2 (Fig. 2e), with a very faint forward trail, possibly due to slight dissociation. The addition of further sulfate had no apparent effect. The change in electrograms from no sulfate ions to 2 SO_4 per Cr_2 suggests a change to a less charged molecule with lower mobility. The mobility of the sulfate complex compared with the 150 gms per liter chrome alum and the violet chrome alum (Fig. 1) would suggest a low positive charge and/or a molecule of at least four chromium atoms. Addition of further sulfate ions in the cold had no effect, and after boiling, there was a slight reduction in the forward trail, but no reduction in the number of cationic complexes as a whole, thus confirming the analytical and spectrophotometric data of the writer [5]

FIG. 2. BASIC COMPLEXES.


(a) POTASSIUM TRIOXALATO CHROMIATE.
(b) BOILED 33 % BASIC CHROMIUM NITRATE.
(c) AS (b) PLUS 1 SO_4 PER Cr_2
(d) AS (b) PLUS 2 SO_4 PER Cr_2
(e) BOILED 33 % CHROME TAN LIQUOR.
(f) AS (e) BUT AGED 6 MTHS.
(g) AS (f) PLUS 1 M/L. K_2SO_4 (NOT BOILED)
(h) AS (g) BUT BOILED
(i) BOILED 50 % BASIC CHROME ALUM
+
-

and presenting a further negation of Gustavson's theory [4] of the neutral salt effect in chrome tanning.

The effect of ageing of the 33 per cent basic chromium sulfate liquor (Fig. 2f) was a small increase in the forward trail, probably due to dissociation of sulfate. There was no sign of a multiplicity of complexes apart from this minor proportion of forward trail, and the presence of a well defined single spot suggests that the majority of the complexes are of a single molecular form.

Although Gustavson [4] has recorded the presence of anionic complexes in the basic chromium sulfates, there was no sign of these on the electrograms. This casts doubt on the use of ion exchangers as an accurate tool in chromium complex analysis.

The 50 per cent basic freshly boiled chromium sulfate complex gave a single well defined spot with a very faint forward trail (Fig. 2i). It was somewhat more mobile than the 33 per cent basic complex.

(c) *Oxalato Sulfate Complex*:

Burley [8] has prepared a green powder by heating to dryness potassium dioxalato chromiate and potassium sulfate. From its spectrophotometric and potentiometric titration curves, and quantitative analysis, he has suggested a mixture of 25 per cent of $K_3 Cr(OX)_2 SO_4$ and 75 per cent of $K_3 (OX)_2 SO_4 H_2O$ the latter having a monodendate attachment of sulfate, giving one free coordination position for H_2O. These complexes decompose in solution to dioxalato chromiate in a few hours at room temperature. Burley's work has been confirmed by Friend [9]. Fig. 3 shows the electrogram of this complex freshly dissolved in iced water, compared with a mixture of potassium trioxalato and dioxalato chromiate.

FIG. 3. MONOSULPHATO-DIOXALATO-Cr.

(a) MIXED POTASSIUM DI + TRI OXALATO CHROMIATES.	+	−
(b) MONO SULPHATO DI OXALATO CHROMIATE.	+	−

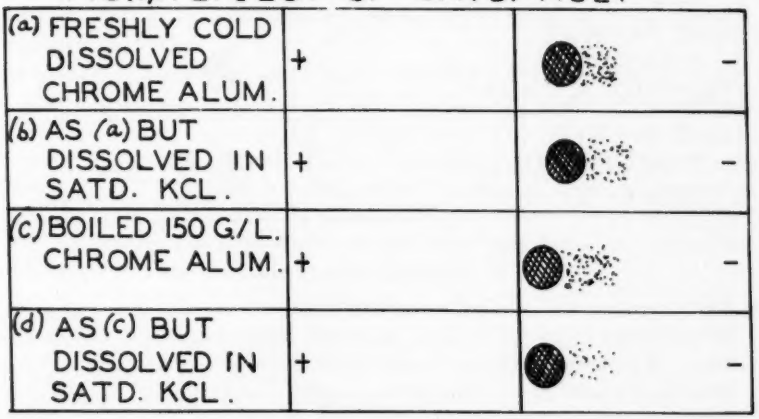
The results are consistent with Burley's data, and are probably due to a mixture of the above two negatively charged oxalato sulfato complexes plus a little dioxalato chromiate produced by decomposition. The green colour of the oxalato sulfate complex was clearly predominant even in the slower moving part of the trail, suggesting that the monodendate sulfate attachment gives a complex of lower mobility than the more symmetrical bidendate sulfate attachment.

(d) *Effect of KCl on Sulfate Co-ordination*:

Atkin [10] has reported that a sulfate-saturated chrome liquor diluted with saturated KCl solution gave no precipitate with benzidine hydrochloride, suggesting that all sulfate had entered the complex. Fig. 4 shows the effect on the complexes of dissolving violet chrome alum in saturated KCl with

and without subsequent boiling, compared with dissolving in water. It is apparent that the KCl has produced no marked effect, although the disappearance of all sulfate would produce anionic complexes. The saturated KCl evidently prevents the precipitate of benzidine sulfate from forming. A similar effect was noted by Burley[8] in work on chromium sulfates in the presence of other electrolytes.

FIG. 4. EFFECT OF SATD. KCL.

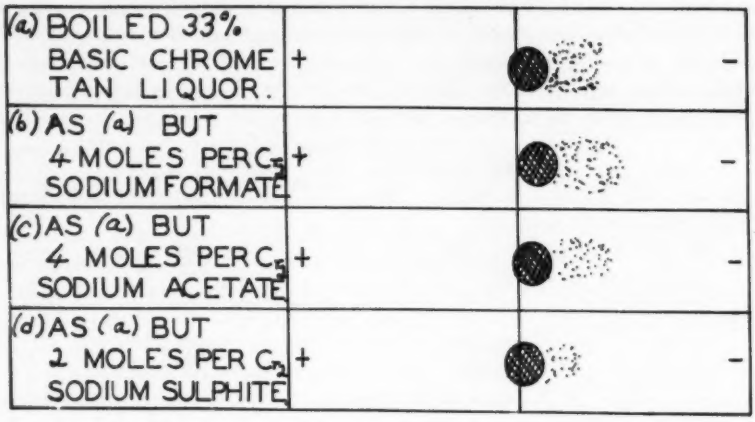


(e) *Effect of masking*:

Theis[11] has suggested that glucose-reduced liquors contain anionic complexes due to the masking action of small quantities of formates, acetates, oxalates, etc., Fig. 5. shows the effects on the complexes of boiling a 33 per cent basic chrome tanning liquor at approximately tan liquor strength with 4 moles per Cr_2O_3 of sodium formate, and sodium acetate, and 2 moles per Cr_2O_3 of sodium sulfite, as compared with the freshly boiled unmasked chrome liquor.

It is evident that all these complexes are cationic, showing that, even with large additions of these masking agents, there has been no production of anionic complexes. In the case of oxalate, the amount present in a glucose-reduced liquor is not sufficient to give anionic complexes, as a minimum of 2 moles per Cr_2O_3 would be needed. It is evident that the tanning properties of these masked complexes have nothing to do with the reduction in number of cationic complexes, but are due to the competitive occupation of available co-ordination positions on the chromium, which modifies the affinity for protein carboxy groups. It is apparent from Fig. 5. that formate was less effective than acetate as a masking agent.

FIG. 5. EFFECT OF MASKING.



General Conclusions

1. The electrographic method shows that chrome alum boiled at 150 g. per liter contains chiefly a uniform positively charged molecule of low mobility. This fits the analytical data of Atkin and Chollett [2] and is at variance with Plant's findings [4]. A very small quantity of more highly charged complexes are present, and ageing in the cold increases this, probably due to dissociation of complex bound sulfate.

2. In the absence of sulfate ions, the one-third basic chromium nitrate appears to consist of a mixture of positively charged olated complexes with one predominating. These complexes are probably the olated dimer containing four positive charges, plus larger olated chains of chromium atoms.

3. At a concentration of 1 per cent Cr_2O_3, an increase in the proportion of sulfate ions up to 4 SO_4 per Cr_2 (as in chrome alum) gradually reduces the apparent mobility of the resultant complex. At this stage the chromium appeared to be mainly in the form of a single complex, positively charged and of low mobility, with a small admixture of more highly charged complexes probably due to dissociation of sulfate. Ageing increased the amount of this minor constituent. The addition of further sulfate had no marked effect either cold or at the boil, supporting the data of the writer [5] and showing that Gustavson's [4] neutral salt theory was based on unsound data.

4. A negatively charged dioxalato mono sulfato chromiate was examined and found to conform in electrographic behaviour with the analytical, spectrophotometric and potentiometric data obtained by previous workers.

5. The effect of dissolving violet chrome alum in saturated KCl solution either cold or at the boil was negligible, although the benzidine hydrochloride method was found by Atkin to show complete absence of ionic sulfate, due to the unsatisfactory nature of the benzidine method in the presence of excess electrolyte as noted by Burley [8].
6. A high level of masking with formate, acetate and sulfite produced only cationic complexes, showing that the effect on tanning of these compounds is not specifically due to a reversal of charge, but is due to the occupation of co-ordination positions by ligands which compete with the protein carboxy groups.
7. A general feature of all these basic chromium sulfate complexes is that after boiling they move as well defined single positively charged spots, showing the probability of uniform molecules. The ion exchange method probably gives erroneous results due to artifacts such as non polar adsorption. All the mobilities were low except those of the oxalato complexes and the non-sulfate-containing basic complexes. However, this was equally true of freshly dissolved violet chrome alum and does not necessarily imply a very large molecule.

References

1. Plant. *J.S.L.T.C.* **32,** 88 (1948).
2. Atkin and Chollet. *J.I.S.L.T.C.* **18,** 356 (1934).
3. Adams. *J.A.L.C.A.* **41,** 552 (1946).
4. Gustavson. *J.A.L.C.A.* **45,** 536 (1950).
5. Shuttleworth. *J.S.L.T.C.* **36,** 34 (1952).
6. Copper. Thesis for M.Sc. Degree, Rhodes University, S. A. 1953.
7. Kunkel and Tiselius . *J. Gen. Physiol.* **35,** 89 (1951).
8. Burley. Thesis for M.Sc. Degree, Univ. of S. A. 1951.
9. Friend. Thesis for M.Sc. Degree, Rhodes University, S. A. 1952.
10. Atkin. *J. Fed. Curriers, Light Leather Tanners and Dressers,* **19,** 175 (1938).
11. Theis and Ganz. *J.A.L.C.A.* **35,** 504 (1940).

Received March 9, 1954

Para-Nitrophenol as a Fungicide for Leather

Robert M. Lollar
(With the Technical Assistance of Helen K. Steinle)*

Dept. of Basic Science in Tanning Research
(Tanners' Council Research Laboratory)
University of Cincinnati
Cincinnati 21, *Ohio*

Nitrophenols exhibit biological activity in a broad spectrum of species. The mono-nitrophenols normally possess a favorable human toxicity index

*This research was partially supported by the Research and Development Division of the Office of the Quartermaster General.

in contrast to the di-nitrophenols. This permits the mono-nitrophenols to be used to control the growth of micro-organisms without excessive hazard to higher animals. Para-nitrophenol is especially efficient in this regard.

This review will consider the organic and physical chemistry of para-nitrophenol, its microbiological activity, and its applicability to the control of fungal growth in the leather industry. It will be seen that leather containing 0.20 to 0.30 per cent para-nitrophenol is resistant to the growth of common molds under very adverse conditions, without causing excessive hazards to the user of such treated leathers. Since para-nitrophenol is readily incorporated into leather and is not prohibitively costly, it is the leather fungicide of choice for many users, and especially for military leathers.

Properties of Para-Nitrophenol

Para-nitrophenol, an odorless, sweetish tasting, colorless to yellow solid, melts at 113-114°C, sublimes and is difficulty volatile in steam (vapor pressure 0.0177 mm). Campbell and Campbell [1], Desvergnes [2], and Sidgwick and Aldous [3] have given fundamental data on the solubility and physical properties of para-nitrophenol. Methanol, acetone, ethanol, and ethyl ether are especially good solvents. Water is a fair solvent, the solubility in grams per 100 centimeters being: 0.80 at 15, 1.6 at 25, 6.1 at 50, 26.9 at 90, and 42.3 at 100°C. Its alkali salts are freely water soluble. It is a fairly strong acid ($K_a = 6.6 \times 10^{-8}$) and possesses pH indicator properties, being colorless in aqueous solutions below pH 5.6 and yellow above pH 7.6. It can be crystallized into two different crystalline modifications; the colorless alpha form crystallizes from toluene above 63°C, while below this temperature the yellowish beta form is secured.

Mixed nitrophenols are readily formed by the action of dilute nitric acid on phenol, with a mixture of ortho–and para-nitrophenol being formed. At very low temperatures, nitration favors the production of para-nitrophenol; at room temperature, the ortho isomer predominates. It is possible to separate the ortho and para isomers by steam distillation, since only the former readily distills. However, it is commercially customary to prepare para-nitrophenol by the action of 15 per cent caustic on para-chloro-nitrobenzene at 160°C during a 4 hour period.

Para-nitrophenol possesses the usual properties expected from its constitution. It can be readily nitrated further, yielding finally picric acid (2, 4, 6 trinitrophenol). Reduction yields para-nitrosophenol and ultimately para-aminophenol. The ethoxy derivative of para-nitrophenol is formed by reaction with ethyl chloride in the presence of sodium hydroxide. Reduction of this ether forms 4-aminophenetole, used in the manufacture of para-ethoxy-acetanilid (acetophenetidine) an analgesic and antipyretic. Thiophosphoryl chloride, sodium ethylate, and sodium para-nitrophenate yield 0, 0 diethyl 0-p-nitrophenyl thiophosphate or Parathion, the new insecticide. These

properties account for the uses of para-nitrophenol as a laboratory chemical and as a pharmaceutical, dye, photographic and insecticide intermediate.

The para positioning of the hydroxy and nitro groups results in para-nitrophenol being quite dissimilar to ortho-nitrophenol. It is a stronger acid, more soluble in water and polar solvents, and less soluble in non-polar solvents, than ortho-nitrophenol. The para isomer is much less volatile than the ortho isomer. The para substitution of the two groups permits inter-molecular hydrogen bonding, while the ortho isomer is intra-molecularly hydrogen bonded; the difference seems to be the cause of the above differences. The meta isomer is intermediate in properties between the other two isomers, but often reflects the greater probability of inter-molecular hydrogen bonding that para-nitrophenol does. Para-nitrophenol forms hydrogen bonded association compounds with such compounds as aniline and para-toluidine. This ability of para-nitrophenol to form intermolecular hydrogen bonded association complexes is probably important in the use of para-nitrophenol as a leather fungicide, since it holds the para-nitrophenol in the leather, minimizing leaching due to use of the leather.

Biological Activity of Para-Nitrophenol

Magne, Mayer, Plantefol, *et al.*[4] have presented data on the pharmacodynamic action of the nitrated phenols. They contrast the poly-nitrophenols to the mono-nitrophenols in that only the poly-nitrophenols convert hemoglobin to methemoglobin, since the actual active agent seems to be an aminonitrophenol. They note that the para-positioning of a nitro and hydroxy group in a compound administered to dogs leads to fever and rapid respiration. Further para-nitrophenol is more toxic to the mold Sterigmatocystis nigra[5] than are the meta and ortho isomers or phenol itself. The polynitrophenols were as toxic or more toxic than para-nitrophenol when evaluated against the mold. Tattersfield, Gimingham, and Morris[6] similarly observed that para-nitrophenol showed more toxicity as a contact insecticide than the other mono-nitrophenols, but less than the poly-nitrophenols. Mazzetti[7] reports that the para isomer is the most active bactericide among the three mono-nitrophenols; Diernhofer[8] has observed that para-nitrophenol exhibits a selective action against Gram negative organisms while permitting Streptococci to grow.

Klemme and Baldwin[9] and Stephens[10] have found that para-nitrophenol will control the development of dermatophytes. Robertson and Marriott[11] report that para-nitrophenol is beneficial in the treatment of skin fungus diseases.

Munson and Yeager[12] have shown that para-nitrophenol leads to a three fold greater rate of kill of roach nymphs than does D.D.T. Many authors have noted interference of para-nitrophenol in embryonic cell development or in enzyme systems.

It is not surprising that a material which is biologically active against such a broad spectrum of organisms should find industrial use. The first use seems to have been on rubber. Pinching [13] and Stevens [14] noted that an 0.15 to 0.30 per cent solution of para-nitrophenol would protect wet rubber against mold growth. Berk [15] has also observed that cork is similarly protected. However, it is probable that the leather industry has used para-nitrophenol more than any other industry. The next section of this paper will trace this use and its development.

The Use of Para-Nitrophenol as a Leather Fungicide

Turner, Musgrave, and Rose [16], in their annotated review of the control of mold growth in the leather industry, note fifteen studies prior to 1948 which attest to the efficiency of para-nitrophenol as a leather fungicide in comparison to other materials. This paper will emphasize the sequence of events which lead to its extensive use in the United States in military leathers.

Blank [17] reported that para-nitrophenol was an especially efficient fungicide in acid media, and recommended its use for the preservation of pickled sheep skins during storage. The next year he noted [18] that para-nitrophenol is very suitable for the protection of moist chrome tanned leather during normal tannery storage. He found that it was three times as effective as beta-naphthol, a common tannery preservative, as the following data show:

Parts per 100 parts of skin	Days of Protection	
	Para-nitrophenol	Beta naphthol
1	5	3
2	14	3
3	14	5

Stuart and Frey [19] confirmed the observation by Blank that para-nitrophenol is effective in controlling the growth of molds on pickled skins. They found that a pickle composed of 12 per cent NaCl, 1.5 per cent H_2SO_4, and 0.025 per cent para-nitrophenol protected skeepskins for 90 days at room temperature even when in contact with moldy cask wood.

Koppenhoefer and Somer [20] found that curing salt containing 0.1 per cent para-nitrophenol held the dissolved volatile nitrogen content of the skin nitrogen to less than 0.1 per cent during a thirty day salting at 30°C, while salt alone gave a volatile nitrogen content of 0.3 per cent of total skin nitrogen.

Doherty [21] compared para-nitrophenol and penta chlorophenol at pH levels of 3, 5, and 7 against Torula species, Neurospora Sitophila, and Fusarium. Para-nitrophenol at a dilution of 1 to 15000 controlled growth of all of the organisms at pH 3 in dextrose broth, but a concentration of 1 to 10000 or higher was required to prevent growth for two weeks at pH 5 and pH 7. Sodium pentachlorophenate was more effective, with a dilution of 1 to 20000

being effective at all pH levels. These laboratory tests were confirmed in plant scale tests on white chrome leather, since these organisms seem to cause a pink discoloration on the finished leather.

Richardson [22] compared para-nitrophenol and sodium pentachlorophenate for their ability to protect chrome leather in the blue at 70°F and at high humidities. The growth on the untreated moist leather occurred in one week or less, while 0.02 per cent of the two additives each protected the leather for 39 days, and 0.10 per cent gave protection for over 50 days.

The trade literature of the Monsanto Chemical Company [23] notes that para-nitrophenol is a good alternative to sodium pentachlorophenate. Their data on the efficiency of various levels of para-nitrophenol in controlling mold growth on chrome tanned leather under practical conditions shows that a 1 to 5000 para-nitrophenol to stock ratio is adequate for tannery protection. They further note that on a cost basis para-nitrophenol is twice as effective as a mixture of phenol and beta-naphthol. Their data reflect the fact that for many years some tanners have used small quantities of para-nitrophenol to control mold growth on chrome leather during tannery processing.

The major impetus to the use of large quantities of para-nitrophenol as a leather fungicide has developed from the need for an agent to protect military leathers from mold growth under humid storage and use conditions. Lollar [24] compared the efficiency of many chemicals for the control of mold growth on leather. He recommended that 0.3 per cent para-nitrophenol was sufficient to protect leather for at least four weeks under severe exposure conditions. Further he found that leather treated with para-nitrophenol was not especially irritating to the skin in small scale tests on dogs, horses, and men. He further found several other agents, including the chlorinated phenols, salicyl anilide and 2-mercaptobenzothiazole, to be effective at similar concentrations. Greene and Lollar [25] simultaneously recommended para-nitrophenol as a component for the dubbin supplied to the U. S. Army during World War II.

During the same period, work on the mold resistance of leather was being conducted also at the U. S. National Bureau of Standards [26] and the Eastern Regional Research Laboratory of the U. S. Department of Agriculture [27]. This work and the study by Lollar was combined in a cooperative test reported by Kanagy, Charles, and Abrams [28]. This article clearly indicated the high comparative efficiency of para-nitrophenol as a leather fungicide. Further, these researches indicated that leather containing as much as 0.25 per cent para-nitrophenol was able to resist mold growth for periods longer than thirty days.

Robertson [29] has reported some very valuable data on the efficiency of para-nitrophenol in the control of mold growth on leather. She states that from 0.14 to 0.30 per cent para-nitrophenol will protect vegetable tanned leather for at least 4 weeks in tropical exposure in West Africa. This British work

also attested to the superiority of para-nitrophenol as a leather fungicide in comparison to several other common fungicides.

The data of Cordon, *et al.* [27] also provide data which show that vegetable tanned leather in the form of binocular cases was protected under Panamanian exposure conditions for approximately three months, if it contained 0.15 to 0.25 per cent para-nitrophenol. Longer exposure resulted in mold growth on the cases. However, cases containing more than 1 per cent of para-nitrophenol or a mixture of para-nitrophenol and salicyl anilide were almost mold-free for nine months of tropical exposure in Panama.

In summary, therefore, it may be said that considerable evidence is available from several sources which prove that para-nitrophenol is able to protect leather against mold growth, and that its efficiency is perhaps better than many of the common preservatives. Further, if the leather contains 0.25 per cent para-nitrophenol it will withstand severe tropical exposure for at least one month and probably for three months. Ultimately, however, the protection is lost probably because the leather loses so much para-nitrophenol, due to leaching.

Any efficient leather fungicide must also be sufficiently non-toxic to man to permit the use in intimate contact with the skin. Hence, before the armed forces made any large scale use of it as a leather fungicide, it was necessary to check rigorously this possibility. The data reported earlier by Lollar [24] represented too few individuals to be conclusive. However, the Office of the Surgeon General conducted extensive toxicity studies which lead to the approval of leather containing 0.2 to 0.4 per cent para-nitrophenol in shoes. Thus, though para-nitrophenol was noted earlier to be microbiologically a fairly active toxic substance, it also is found to be sufficiently non-toxic to man to make its use in leather feasible. Of course, those who regularly handle it in the production of leather should exercise the customary precautions in the handling of toxic chemicals. However, the experience of the industry over many years is proof that this is not impossible.

The earliest required uses of para-nitrophenol as a preservative agent for leather were contained in specifications for leather treating compounds. Specification JAN-C-1063, 11 April 1949, is equivalent to U. S. Army Specification 92-61, 11 December 1945, which was preceded by AXS 1416, 26 September 1944, and EBP No. 877, 19 July 1945. This formula is composed of 2 per cent para-nitrophenol, ten per cent each of animal and hydrocarbon oil, 10 per cent cyclohexanone, and 68 per cent perchlorethylene. Federal Specification OL-164a, 25 March 1952, and first adopted 21 February 1949, includes the same formula. In addition, it includes a second composition containing 5 per cent para-nitrophenol in sulfonated cod or neatsfoot oil. Military Specification, MIL-L-10095, 17 January 1950, MIL-L-10331 (Ord.), 31 May 1950, and General Service Administration Specification No. 2130,

21 February 1951, are similar to OL-164. The earliest specification of this type seems to have been AXS-1672, 21 July 1945.

During the latter half of 1950, it was decided that all leathers procurred by the Office of the Quartermaster General should contain 0.3 per cent para-nitrophenol. It was estimated that this would require a minimum of 600,000 pounds of para-nitrophenol per year. This volume of para-nitrophenol was not readily available to the leather industry; hence, it was not mandatory that para-nitrophenol be added until October, 1951. While the original permissable range was 0.2 to 0.4 per cent, the specification limits were subsequently narrowed to 0.2 to 0.3 per cent, and are now set at 0.18 to 0.35 per cent for shoe leather.

The Analysis of Leather for Para-Nitrophenol

The production and procurement of leather containing para-nitrophenol to meet these narrow specification limits requires an analytical method to determine the leather's content of para-nitrophenol. The method should be sufficiently specific to differentiate para-nitrophenol from the other phenolic and/or nitrogen containing components likely to be found in leather. Ideally, the method should not report other nitrophenols, since the specification permits only para-nitrophenol and the several nitrophenols differ in the efficiency with which they control microbic growth.

Lollar[30] has reported on a method which possesses these requirements. The method as published extracts the para-nitrophenol along with the grease from the leather by chloroform. The extracted para-nitrophenol is reduced to para-aminophenol by the action of titanous chloride. The para-aminophenol is coupled with phenol to yield an indophenol blue color which color is proportional to the para-nitrophenol in the leather extract. The method is so specific that only para-nitro and para-aminophenols will yield the blue color. The para-aminophenols can be distinguished from the para-nitrophenols by eliminating the reduction stage; only the para-aminophenols yield the blue color without reduction. Ortho-and meta-nitrophenol do not interfere.

Other methods are available for the determination of para-nitrophenol in leather. Lollar[30] has discussed some of these which had been published prior to his article. Marine Corps Specification MIL-S-17338 MC, 28 August 1952, determines para-nitrophenol in service shoe leather by a Kjeldahl nitrogen analysis of the sodium carbonate extraction of the leather. This method is not specific since many nitrogen containing substances including dyes, finishes and amine emulsifiers are extractable from the leather with sodium carbonate. Further, it requires a microburrette titration for adequate precision in the Kjeldahl method. Also the precision of the Kjeldahl method is not always adequate.

Specification MIL-B-11077 QMC, 12 April 1951, covers the use of the Kjeldahl method on the chloroform extract from leather. This method suffers

from the same defects noted with respect to MIL-S-17338. As a result, the indophenol blue colorimetric method described by Lollar has received more extensive use.

The use of the indophenol blue method of analysis necessitated careful study of the method to find the procedural points requiring the most care to secure concordant results. Each detail of the method as published has been reviewed to determine its influence on the precision of the method. It has been found that the titanous chloride stock solution should be carefully stored in the cold and out of contact with air. The dilution water should be freshly boiled and cooled to 80°C, before use as a diluent. These precautions yield a clear dark purple dilute titanous chloride of good reducing efficiency. The pH during color development was also found to be fairly critical, with somewhat more precise results being secured if the pH is at the specified value of 9.6±0.1 pH.

TABLE I

The Effect of Elapsed Time on Indophenol Blue Color Development
Data are Optical Density x 1000

Time Elapsed Minutes	Theoretical % pNP on Leather Basis					
	0.1		0.2	0.3	0.5	
	Day 1	Day 2	Day 1	Day 1	Day 1	Day 2
PART A: TIME ELAPSED BETWEEN BORATE BUFFER AND PHENOL						
0	202	209	407	611	1010	1030
	201	208	408	615	1020	1050
15	197		385	578	918	
	189		372	563	919	
30	153		313	475	780	
	162		313	465	732	
60	93	80	194	301	528	425
	87	78	203	306	516	438
PART B: EFFECT OF COLOR DEVELOPMENT TIME AFTER PHENOL ADDITION						
30	122		294	444	789	650
			315	475		
60	187		400	600	963	980
			406	608		
90	205		413	611	995	
			413	611		
120	207		410	607	1050	999
			412	607		
150	207		406	610	1060	
			406	610		
200	206		400	610	1020	980
			407	609		

The timing of the method can be made more precise to improve the reproducibility of the results. The time elapsed up to the addition of the

borate buffer is not critical. However, after the borate buffer has been added, the phenol should be added immediately. A delay before the addition of

TABLE II

The Analysis of Leather for Para-Nitrophenol by Indophenol Blue Assay
Data are in Per Cent

Leather	Extraction Solvent	Replicate H_2P Content	B 1	B 2	P 1	P 2	T 1	T 2	Totals
E	$CHCl_3$	Air Dry	0.27	0.36	0.30	0.35	0.26	0.28	
			0.26	0.28	0.30	0.35	0.25	0.28	3.54
	$CHCl_3$	Moist	0.46	0.48	0.48	0.45	0.47	0.47	
			0.46	0.48	0.48	0.45	0.47	0.47	5.62
	EtOH	Air Dry	0.43	0.46	0.51	0.50	0.46	0.48	
			0.43	0.46	0.50	0.49	0.46	0.48	5.66
	E Sub-Totals		2.31	2.52	2.57	2.59	2.37	2.46	14.82
H	$CHCl_3$	Air Dry	0.24	0.26	0.32	0.31	0.25	0.26	
			0.25	0.27	0.32	0.29	0.22	0.28	3.27
	$CHCl_3$	Moist	0.33	0.36	0.35	0.33	0.34	0.34	
			0.33	0.36	0.35	0.33	0.34	0.34	4.10
	EtOH	Air Dry	0.33	0.35	0.37	0.37	0.34	0.36	
			0.33	0.35	0.36	0.37	0.34	0.36	4.23
	H Sub-Totals		1.81	1.95	2.07	2.00	1.83	1.94	11.60
51	$CHCl_3$	Air Dry	0.26	0.25	0.30	0.27	0.24	0.27	
			0.26	0.25	0.30	0.28	0.22	0.27	3.17
	$CHCl_3$	Moist	0.31	0.30	0.31	0.32	0.28	0.30	
			0.31	0.31	0.31	0.32	0.29	0.30	3.66
	EtOH	Air Dry	0.28	0.30	0.31	0.30	0.30	0.31	
			0.28	0.31	0.32	0.32	0.32	0.32	3.67
	51 Sub-Totals		1.70	1.72	1.85	1.81	1.65	1.77	10.50
Solvent Sub-Totals	$CHCl_3$	Air Dry	1.54	1.67	1.84	1.85	1.44	1.64	9.98
	$CHCl_3$	Moist	2.20	2.29	2.28	2.20	2.19	2.22	13.38
	EtOH	Air Dry	2.08	2.23	2.37	2.35	2.22	2.31	13.56
Replicate Sub-Totals			5.82	6.19	6.49	6.40	5.85	6.17	36.92
Laboratory Sub-Totals			12.01		12.89		12.02		36.92

phenol will cause less color to develop. Further, it was found that approximately two hours for color development after the addition of the borate phenol reagents was desirable for optimum color development. Table I shows the data which support these conclusions.

The major error was found to be involved in the extraction procedure to remove the para-nitrophenol from the leather. After the method has been used by several industrial laboratories, it was found that variations of 0.1 per cent or more were being observed which seemed to be due to laboratory error. Extensive study in many laboratories, but particularly in the Endicott-Johnson Shoe Company, the Philadelphia Quartermaster Depot, the Bureau of Standards Leather Section, and the Tanners' Council Laboratory, revealed that dry chloroform incompletely extracted air dry leather, but that chloroform would do a better extraction on wet leather and that ethanol was a superior extractant on air dry leather. However, it was found that the tannins extracted by alcohol interfered in the method so that it was necessary to precipitate them with lead acetate before using the para-nitrophenol method. To compare these methods, a collaborative experiment was performed, yielding the data in Tables II and III.

TABLE III

Variance Analysis of the Para-Nitrophenol Assay Data

Source of Variance	Degrees of Freedom	Crude Square	Mean Square	Component of Variance	F-Value	Significance Level
Extraction	3–1=2	0.2800	0.1400	0.00516	232	0.001
Laboratory	3–1=2	0.0141	0.00705	0.00024	11.6	0.001
Leather	3–1=2	0.2260	0.1130	0.00416	187	0.001
Extn. x Lab.	2x2=4	0.1101	0.00252	0.00014	4.17	0.05
Extn. x Lea.	2x2=4	0.0779	0.01948	0.00140	32.3	0.001
Lab. x Lea.	2x2=4	0.0003	0.000075	Insig.	0.12	Insig.
Extn. x Lab. x Lea.	2x2x2=8	0.0038	0.000475	Insig.	0.79	Insig.
Replicates	27(2–1)=27	0.0163	0.000604	0.000604	—	—
Chemist's Duplicates	54(2-1)=54	0.0053	0.0001	—	—	—
TOTAL	108-1=107	0.6338	—	—	—	—

The three leathers selected represented two different chrome retanned vegetable insole leathers (E and H) and one stuffed retan army shoe upper

leather (No. 51). The three extraction procedures were: dry chloroform extraction on air dry leather as originally recommended by Lollar[30]; moist chloroform extraction resulting when leather moistened with its own weight of water was extracted with chloroform; ethanol extraction followed by lead acetate precipitation of the tannins giving the third set of data. The three laboratories selected were each equipped to measure the developed color instrumentally. Each laboratory replicated their data by extraction of the leather on two different days with different extractions, standard curves and analysts, but the same equipment and general laboratory interpretations of the procedures. Thus, these are deemed to be statistical replicates. In addition each replicate was duplicated in the chemists sense in that two independent extractions and color developments were run side by side on each leather and solvent in each statistical replicate. The raw data comprise Table II while Table III presents the statistical analysis of the data.

The statistical analysis must follow a particular peculiar program. First, since the chemists duplicates are not statistical replications, the variance due to them was removed from the total variance. Then the remaining data comprise a three factor with two-fold replication factorial experiment. This analysis of variance regards the three levels of the three factors as complete populations; so that the analysis described by Villars[31] in Table 7, 3, 6a is appropriate; the replicate mean square is therefore the error variance for all variance sources.

Either Table II or Table III will demonstrate that the three different extraction procedures have given different para-nitrophenol analysis. Further, it is noted that the concordance of the three laboratories is best with the moist chloroform extraction.

This results in the significant extraction x laboratory interaction in Table III. Since the assay procedure is specific, the highest assay is the most accurate assay. It is noted that either the ethanol extraction of the air dry leather or the chloroform extraction of the wet leather gives comparable and higher para-nitrophenol values than the use of chloroform on air dry leather. Further, the chloroform extraction of the wet leather is simpler since it does not require the lead acetate precipitation of the tannins. Hence, the chloroform extraction of the wet leather is the preferable extraction procedure.

Some Problems in the Application of Para-Nitrophenol to Leather

The solubility of para-nitrophenol in water is such that it is impractical to add it to leather from a water solution if one desires to secure the required military level of 0.25 per cent. However, it is sufficiently soluble in several organic solvents to permit their use in incorporating para-nitrophenol into leather; this is especially true of the more polar solvents such as the alcohols or ketones. These solvents are used advantageously in the several military specifications mentioned earlier. Kremen, working in this laboratory, also

developed a process to improve finished insole leather which takes advantage of the solubility of para-nitrophenol in isopropyl alcohol. He recommends this approximate formula for use on 100 pairs of cut soles:

Para-Nitrophenol	0.75 lb.
Raw Neatsfoot Oil	6.0 lb.
Mineral Oil	3.0 lb.
Isopropyl alcohol	28.0 gals.
Formalin (37% HCHO)	1.0 gal.

Immersion of wet insoles in this formula for from 3 to 18 hours yields a piece of leather with increased perspiration stability due to the formaldehyde retannage and with mold resistance due to the para-nitrophenol. After drying the finished cut soles are practically indistinguishable from the untreated leather with regard to color, firmness, weight, thickness, size, shape, and planarity. The solution may be reused after replenishment. Surface treatments of finished leather goods are also possible with this and similar formulae by spray applications. The ability of leathers to take up para-nitrophenol from these solutions as well as from water seems to indicate some adsorptive force, possibly hydrogen bonding, since the uptake of the para-nitrophenol may exceed the uptake of other components of the solution.

However, it is customary for the tanner to incoporate the para-nitrophenol into the leather during lubrication. Merrill[32] has published data on the solubility of commercial para-nitrophenol in oils and greases. As both Merrill and Koppenhoefer[33] note, para-nitrophenol possesses the ability to increase the sludging characteristics of many oils and greases. Hence, it is desirable to hold para-nitrophenol containing greases at elevated temperatures for the minimum period to secure solution and incorporation into the leather. Fatty oils such as tallow or neatsfoot oil and sulfated oils are especially good solvents while the mineral oils and hydrocarbons are very poor solvents.

The tanner has a problem in incorporation in that the uptake of fats by the leather is not completely uniform from area to area in the same side and from side to side. This is not particularly significant in terms of leather properties unless the non-uniformity becomes excessive. However, the narrow specific limits for para-nitrophenol set by the military specifications make it very difficult to hold the required para-nitrophenol level. This is particularly true when the magnitudes of the analytical errors noted in Table II are recalled.

An additional practical problem due to the use of para-nitrophenol in military leathers arises in those leathers which are used partially by the civilian leather trade and partly in military leathers. It is often impractical to prepare the leather both with and without para-nitrophenol. Hence, the civilian leather also must contain para-nitrophenol. The cost of this is offset

to some extent by the fact that no other fungicide will be needed to protect the leather in the tannery and by the fact that the leather will be mold free when in the consumer's hands. However, when such leather is in contact with alkaline pastel colored substances for some time, a yellowing of the alkaline substance due to para-nitrophenol will be observed. Thus, formaldehyde tanned white shoe uppers in contact with para-nitrophenol containing insoles and soles will yellow around the sole attachment area. Light colored men's suits have shown a yellow streak under a para-nitrophenol containg belt after being in a show window. This color is due to para-nitrophenol transfer and can be bleached by acid vapors. However, the color will always be visible whenever the surface is alkaline.

The toxicity of para-nitrophenol is such that tanners are advised to require good hygienic and safety practices from all workers who apply para-nitrophenol to the leather or handle the wet leather containing it. The dusting or volatilization of para-nitrophenol into the air should be avoided. Proper protective clothing and frequent thorough washing with soap are advised for all workmen. However, the chemical is not sufficiently hazardous so that it cannot be used in a tannery, as twenty years of such use will attest. The dry leather is safe as long as the contact with the skin is not direct and intimate over long periods of time, and as long as the leather content of para-nitrophenol is not excessive. The Surgeon General desires that not more than 0.4 per cent be present.

The Effect of Para-Nitrophenol on Leather Age Deterioration

Para-nitrophenol was added to military leathers to control the growth of molds. This is sufficient to justify the use of a fungicide. Further, it was observed that military shoes not containing para-nitrophenol underwent severe deterioration when stored in humid climates. Koppenhoefer[33] concluded that this deterioration was due to the growth of the molds. However, other workers suggested that para-nitrophenol might itself deteriorate leather. It was therefore decided that some data should be secured on the role of para-nitrophenol in the storage stability of leather.

Tanners of chrome vegetable retan shoe upper leather under military specification MIL-L-3122 were invited to submit samples of their leathers with and without para-nitrophenol. This request was made in the late summer of 1951 when the use of para-nitrophenol was just being adopted for military leathers. Hence, each tanner was requested to sample randomly six sides of his leather with and without para-nitrophenol; the sampling location was that to the rear of the kidney, recommended by Mann *et al.*[34] for sampling of leather. The one-foot square blocks were cut into five portions. One portion was submitted to immediate chemical analysis and physical testing. Three portions were stored for one year in the three different climatization cabinets of the Philadelphia Quartermaster Depot. These three

climates represent temperate summer, desert dry, and tropical moist climates. The fifth portion was stored for ten months in an atmosphere modified from the A. L. C. A. mold resistance test environment[8,5]. It differed from the tropical moist storage in that the atmosphere was always at 100% R. H. at 35°C while the tropical moist climate involved a cycle including a lower humidity period during part of each day. After the storage period, the portions were removed, freed of any mold by swabbing with water, and reconditioned for analysis and testing. The procedures used in testing were those specified in KK-L-311, dated 28 March 1945. Two exceptions were made in the procedure. First, all shrinkage temperatures were performed in water as the heat transfer medium. Burst strength data were secured with a 1/8 inch diameter hemispherical steel ball driven by a hydraulic cylinder. The hydraulic pressure to rupture of the leather was reported as the ball burst pressure. All equipment and procedures were used by the same analyst for all of the testing so that instrumental and operator errors were minimized.

TABLE IV

The Effect of Aging on Stitch Tear Strength

The data shown are the sum, in pounds,
of the force required to tear the leather—two hole test.

Each figure is the sum from 6 specimens.

Treatment		Control	Temp. Storage	Desert Storage	Moist Storage	Mold Test	
Tanner	Para-Nitrophenol	no storage	1 year	1 year	1 Year	100% R. H. 10 Mo.	Totals
A	+	497	467	440	420	333	2157
	—	422	380	372	309	205	1688
V	+	366	379	383	294	148	1570
	—	423	370	439	324	151	1707
I	+	468	378	353	328	288	1815
	—	515	374	407	370	209	1875
S	+	553	545	540	480	283	2401
	—	537	567	546	520	379	2549
D	+	413	435	451	433	278	2010
	—	460	414	404	399	252	1929
TOTALS		4654	4309	4335	3877	2526	19701

TABLE V

The Effect of Aging on the Ball Burst Strength

The data shown are the sum, in pounds, of the pressure to push a ⅛ inch diameter ball through the leather

Each figure is the sum from 6 specimens

Treatment		Control	Temp. Storage	Desert Storage	Moist Storage	Mold Test	
Tanner	Para-Nitrophenol	no storage	1 Year	1 Year	1 Year	100% R. H. 10 Mo.	Totals
A	+	437	504	441	443	318	2145
	—	388	372	365	311	314	1750
V	+	332	311	316	226	166	1351
	—	401	360	381	290	245	1677
I	+	453	376	386	337	279	1831
	—	432	467	446	352	289	1986
S	+	523	459	494	413	397	2286
	—	667	574	599	510	471	2821
D	+	414	420	427	394	306	1961
	—	411	391	419	409	347	1977
TOTALS		4458	4234	4274	3685	3132	19783

Tables IV and V show the effect of the aging on the stitch tear strength and ball burst strength, in pounds, of the leathers as received and after the four aging procedures. The data are recorded as the pounds to tear since it was found that the linear correlation between the pounds to failure and the thickness was not statistically significant. This is in agreement with the results reported by Mitton, who states that it is erroneous to divide stitch tear breaking loads by thickness [3 6]. To simplify these tables, the sums of the six values from the six specimens from the six sides are recorded in each cell of Tables IV and V. Table VI presents the analysis of variance of the data summarized in Tables IV and Table V.

It is obvious from both statistical and intuitive examination of the data that the age deterioration of the leather is significant. This is especially true of the leathers aged in the moist tropical climatization room and the mold resistance test. This suggests that the deterioration is a hydrolytic deterioration.

TABLE VI

The Aging of Variance of the Effect of Aging on the Strength of Leather

Source of Variance	Degrees of Freedom	Stitch Tear Strength				Ball Burst Strength			
		Crude Square	Mean Square	F Value	Signif. Level	Crude Square	Mean Square	F Value	Signif. Level
Tanner	5–1=4	25519	6380	59.1	0.001	36827	9207	43.3	0.001
pNP Level	2–1=1	139	139	1.3	Insig.	1361	1361	6.4	0.05
Aging	5–1=4	46755	11689	108	0.001	19714	4928	23.2	0.001
T x pNP	4x1=4	4375	1094	10.1	0.001	7159	1790	8.4	0.001
T x A	4x4=16	4436	277	2.6	0.01	2736	171	0.8	Insig.
pNP x A	1x4=4	402	100	0.9	Insig.	193	48	0.2	Insig.
T x pNP x A	4x1x4=16	2194	137	1.3	Insig.	2962	185	0.9	Insig.
Replicates	2x5(6-1)=50	27076	108	—	—	53348	213	—	—
TOTAL	300-1=299	110896	—	—	—	124300	—	—	—

It is also true, although not so obvious, that the presence or absence of para-nitrophenol is not a major factor in establishing the deterioration of the strength of the leather. In the mixed inoculum mold resistance test, all of the control leathers molded freely in a month or so after the storage period was started. The para-nitrophenol treated leathers were mold free except those that contained less that about 0.1 per cent para-nitrophenol. In the climatization rooms the conditions were not sufficiently severe to mold many of the samples. When we examine the statistical analysis of the strength data, we note that the para-nitrophenol level did not influence the stitch tear strength of the leather. The significant level for ball burst strength, calculated for the influence of the para-nitrophenol level, is really the result of the very strong leather without para-nitrophenol which tanner S submitted. It happened that five of his six sides were among the strongest of all the sides submitted. This effect therefore seems to be a sampling error.

Table VII presents the chemical analysis of the composited leather from the physical test specimens for each cell of the experiment. It will be noted that the para-nitrophenol free leather has lost grease extensively from aging in the moist resistance test; however, the leathers which were protected with para-nitrophenol or which did not mold due to the storage conditions being unfavorable did not lose grease. Further, there is a lesser tendency for the chrome oxide and nitrogen to increase on the as-received basis, which seems

TABLE VII

The Effect of Aging on the Chemical Analysis of the Leather

Tanner	A		V		I		S		D	
Age Factor pNP	+	—	+	—	+	—	+	—	+	—
PARA-NITROPHENOL (%–AS IS BASIS)										
Original Leather	0.24	—	0.21	—	0.20	—	0.09	—	0.20	—
Temperate Summer	0.22	—	0.19	—	0.17	—	0.06	—	0.20	—
Moderate Desert	0.22	—	0.20	—	0.17	—	0.06	—	0.18	—
Tropical Moist	0.19	—	0.18	—	0.15	—	0.06	—	0.17	—
Mold Test	0.13	—	0.11	—	0.09	—	0.01	—	0.10	—
CHROME OXIDE (% Cr_2O_3–DRY BASIS)										
Original Leather	2.30	2.25	2.75	2.45	3.45	2.70	2.80	2.65	2.25	2.15
Temperate Summer	2.49	2.39	3.00	2.43	3.55	2.58	2.83	2.75	2.42	2.41
Moderate Desert	2.34	2.06	2.99	2.69	3.59	2.98	2.77	2.74	2.48	2.20
Tropical Moist	2.34	2.39	2.42	2.73	3.62	2.89	2.83	2.78	2.52	2.38
Mold Test	2.42	2.78	2.88	3.32	3.49	2.79	3.43	3.31	2.50	2.79
NITROGEN BY KJELDAHL METHOD (%N–AS IS BASIS)										
Original Leather	8.01	7.93	7.52	7.56	8.42	8.43	7.96	8.29	8.51	8.35
Temperate Summer	8.53	8.01	7.84	7.54	8.54	9.10	7.94	8.43	8.76	8.37
Moderate Desert	8.68	8.46	7.86	8.13	8.93	9.34	8.10	8.15	9.08	9.04
Tropical Moist	8.64	8.23	7.55	8.00	8.87	9.20	7.52	8.27	8.93	8.70
Mold Test	8.65	8.64	7.76	8.83	8.93	9.34	8.78	8.81	8.76	9.18
GREASE (% $CHCl_3$ EXTRACTIVE–AS IS BASIS)										
Original Leather	18.6	17.7	22.0	23.6	17.3	15.8	19.5	19.6	19.0	17.1
Temperate Summer	17.6	17.9	19.9	21.0	17.1	16.3	20.2	19.4	18.7	18.3
Moderate Desert	18.0	17.3	22.2	22.9	16.0	16.0	21.1	21.0	17.8	16.4
Tropical Moist	17.2	17.5	21.7	22.6	15.5	16.1	21.3	20.5	17.5	16.6
Mold Test	16.3	3.4	20.1	5.4	16.1	2.3	6.1	9.35	17.5	3.5
pH OF LEATHER EXTRACT										
Original Leather	3.10	3.15	3.32	3.33	3.15	3.08	3.38	3.27	2.92	2.88
Temperate Summer	3.15	3.21	3.40	3.45	3.18	3.09	3.49	3.38	3.02	3.09
Moderate Desert	3.18	3.18	3.39	3.37	3.19	3.09	3.47	3.38	3.02	3.02
Tropical Moist	3.19	3.22	3.42	3.36	3.10	3.04	3.58	3.39	2.98	3.01
Mold Test	2.99	2.78	3.13	2.98	2.89	2.75	3.14	2.99	2.88	2.81
SHRINKAGE TEMPERATURE OF LEATHER (°C IN WATER)										
Original Leather	3	3	3	3	3	3	3	3	3	3
Temperate Summer	3	3	94	94	98	95	3	3	95	95
Moderate Desert	91	89	88	83	92	89	96	92	85	81
Tropical Moist	3	3	96	94	95	94	3	98	94	95
Mold Test	94	90	87	84	93	90	91	90	91	87

"3" denotes that specimens withstood 3 minutes boil test

to be due to a loss of vegetable extract during storage. This was certainly true during the A. L. C. A. mold resistance test. Further, the mold resistance test conditions have produced a significant decrease in the leather pH.

The most surprising change in the leather is the change in the shrinkage temperature of the leathers. All of the aging procedures have produced real decreases in shrinkage temperature. Again, however, the deterioration is greatest in the mold resistance test, and the presence or absence of para-nitrophenol to control mold growth has only a minor influence.

These results are in general agreement with those of Kanagy *et al.*[26] and Mitton *et al.*[37] on vegetable leather. They attribute the influence of mold on leather primarily to the removal of water solubles and grease and show minimal influence of the leathers strength as a result of mold growth.

The strength deterioration noted here is however greater than the strength deterioration reported by these authors. However, the storage times in securing these data are about twice as long as those reported previously and the temperature in the mold resistance test was higher than their temperature. Both of these factors would accentuate a hydrolytic deterioration. Further, it may be that the retan leathers are more unstable than vegetable tanned leathers. In any event, the results agree with the reported results of tropical storage of shoes made from this type of leather.

These results agree with Koppenhoefer's conclusion[33] that the growth of molds on the leather can cause grease loss. However, it is not true that the grease loss is the entire cause of the strength loss of the leather. Rather, it seems that the humid conditions necessary for mold growth also induce a hydrolytic deterioration of the leather due to the water content of the leather and its temperature. Unpublished data on other leathers show that this deterioration is much less severe at 20°C than it is at 35 or 40°C.

It might be noted that other tanners submitted samples for this study. However, due to failure to submit both treated and untreated leather, or due to failure to sample the leather properly, or to errors in para-nitrophenol addition, only these five tanners leathers could be included in the data presented here. However, the qualitative observation was the same in that the presence of 0.2 per cent para-nitrophenol was adequate to prevent mold growth and consequent grease loss; however, the leather still deteriorated in strength due to hydrolytic deterioration. In the overall picture, fifty sides with para-nitrophenol were tested to support these conclusions. Further, these fifty sides disclosed no evidence that the presence of para-nitrophenol was in any way harmful to the properties of the leather.

Summary

The value of para-nitrophenol as an industrial fungicide, and specifically as a leather fungicide, has been reviewed. It is shown that leather containing at least 0.2 per cent para-nitrophenol will remain mold free for at least three

months in tropical exposure and at least 10 months in humid storage at 35°C and almost saturated humidity.

The presence of para-nitrophenol in the leather will prevent the loss of grease in retan leather, which seems to be consumed by the molds. However, the leather will still deteriorate during humid storage, since the loss in physical strength seems to be due to an independent hydrolytic deterioration mechanism. Hence, though the use of para-nitrophenol to control mold growth is justified because it does do this, it must not be expected to protect the strength of the leather during improper humid storage.

The indophenol blue assay for para-nitrophenol in leather has been examined in detail and improved in precision over the originally published method. Some of the problems to be expected with para-nitrophenol containing leathers are also discussed.

Acknowledgments

This paper required the cooperation of many organizations. The author would like to extend his thanks to the American Hide and Leather Company, the Armour Leather Company, Beggs and Cobb, Incorporated, Eagle Ottawa Leather Company, Endicott-Johnson Corporation, International Shoe Corporation, Irving Tanning Company, Northwestern Leather Company, Pfister and Vogel Tanning Company, and Seton Leather Company.

In addition the cooperation of the laboratories of the Philadelphia Quartermaster Dept. and the Bureau of Standards Leather Section was valuable.

Bibliography

1. Campbell, A. N., and Campbell, A. J. R., *Can. J. Res.* **19B,** 73 (1941).
2. Desvergnes, Louis, *Rev. chim. ind.* **36,** 194 & 224 (1927).
3. Sedgwick, N. V., and Aldous, W. M., *J. Chem. Soc.* **119,** 1001 (1921).
4. Magne, Henry, Mayer, A., Plantefol, L., *et. al., Ann. physid. physicochim biol* **8,** lffd (1932).
5. Plantefol, L., *Compt. rend.* **174,** 123 (1922).
6. Tattersfield, F., Gimmingham, G. T., and Morris, H. M., *Annals App. Biol.* **12,** 218 (1925).
7. Mazzetti, G., *Boll. Soc. Ital. biol. sper.* **6,** 1108 (1931).
8. Diernhoefer, K., *Milch. Forsch.* **18,** 83 (1936).
9. Klemme, Dorothea E., and Baldwin, Agnes C., *U. S. Dept. Agric. Circular* No. 758 (1947).
10. Stephens, Frances L., *J. Roy. Nav. Med. Serv.* **27,** 273 (1941); *Trop. Diseases Bull.* **39,** 103 (1942).
11. Robertson and Marriott, *Brit. Med. J.*, 136 and 1339 (1935).
12. Munson, S. C., and Yeager, J. T., *J. Econ. Entomol.* **38,** 618 (1945).
13. Pinching, H. C., *Bull. Rubber Growers Assoc.* **6,** 545 (1924).
14. Stevens, H. P., *Bull. Rubber Growers Assoc.* **6,** 635 (1925); **7,** 108, 243, and 419 (1925).
15. Birk, Sigmund, *A. S. T. M. Bulletin*, p. 73 (1947).
16. Turner, J. N., Musgrave, A. J., and Rose, C. D., *J. Soc. Leather Trades Chem.* **32,** 104, 127 (1948).
17. Blank, I. H., *J. Amer. Lea. Chem. Assoc.* **27,** 380 (1932).

18. Blank, I. H., *J. Amer. Lea. Chem. Assoc.* **28,** 583 (1933).
19. Stuart, L. S., and Frey, R. W., *J. Amer. Lea. Chem. Assoc.*, **29,** 113 (1934).
20. Koppenhoefer, R. M., and Somer, G. L., *J. Amer. Lea. Chem. Assoc.* **34,** 34 (1939).
21. Doherty, E. E., *J. Amer. Lea. Chem. Assoc.* **34,** 464 (1939).
22. Richardson, J. F., *Hide and Leather and Shoes,* May 11, 1940.
23. "Chemicals for the Tanning Industry," a booklet published by the Monsanto Chemical Company, pages 12–13.
24. Lollar, Robert M., *J. Amer. Lea. Chem. Assoc.* **39,** 12, 179, 203 (1944).
25. Greene, H. S., and Lollar, Robert M., *J. Amer. Lea. Chem. Assoc.* **39,** 209 (1944).
26. Kanagy, J. R., Charles, A. M., Abrams, E., and Tener, R. F., *J. Amer. Lea. Chem. Assoc.* **41,** 198 (1946).
27. Cordon, T. C., Rogers, J. S., Mann, C. W., and Teitell, L., *J. Amer. Lea. Chem. Assoc.* **44,** 472 (1949).
28. Kanagy, J. R., Charles A. M., and Abrams, E., *J. Amer. Lea. Chem. Assoc.* **43,** 14 (1948).
29. Robertson, Madge E., "Progress in Leather Science," p. 114 (1948). Published by British Lea. Mfg. Res. Assoc., London, England.
30. Lollar, Robert M., *J. Amer. Lea. Chem. Assoc.* **50,** 728 (1950).
31. Villars, D. S., "Statistical Design and Analyses of Experiments for Development Research," Em. C. Brown Co., Dubuque, Iowa. 1951.
32. Merrill, H. B., *Shoe and Leather Reporter,* August 18, 1951.
33. Koppenhoefer, R. M., *Shoe and Leather Reporter,* p. 23, September 15, 1951.
34. Mann, C. W., Mandel, J., Steel, Mary, and Kanagy, J. R., *J. Amer. Lea. Chem. Assoc.* **47,** 370 (1952).
35. Amer. Lea. Chem. Assoc. Methods of Testing. Method E34. Methods securable through office of the Secretary, University of Cincinnati, Cincinnati 21, Ohio.
36. Mitton, R. G., *J. Soc. Lea. Trades Chem. Soc.* **37,** 65 (1953).
37. Mitton, R. G., Musgrave, A. J., *J. Amer. Lea. Chem. Assoc.* **34,** 324 (1950), **35,** 82 (1951).

Received October 8, 1953

An Insole Leather Tester

I. D. Clarke and R. M. Flaharty

Eastern Utilization Research Branch
Agricultural Research Service
U. S. Department of Agriculture

During the war, the need for insole leather of better quality became evident. Work on the improvement of this type of leather made desirable, or even necessary, a rapid laboratory method for testing insole quality. Machines for this purpose have been devised and described [1, 2]. A machine which performs essentially the same operation as those referred to, that is, one which flexes leather under pressure, has been devised, built and used in this laboratory, and is described briefly here because it has been used to determine the relative durability of vegetable–and alum–retanned insoles [3].

The machine, without the cover for retaining heat and moisture, is shown in Figure 1. Four specimens can be flexed at one time. Figure 2 shows the working parts involved in flexing a specimen and applying pressure to it.

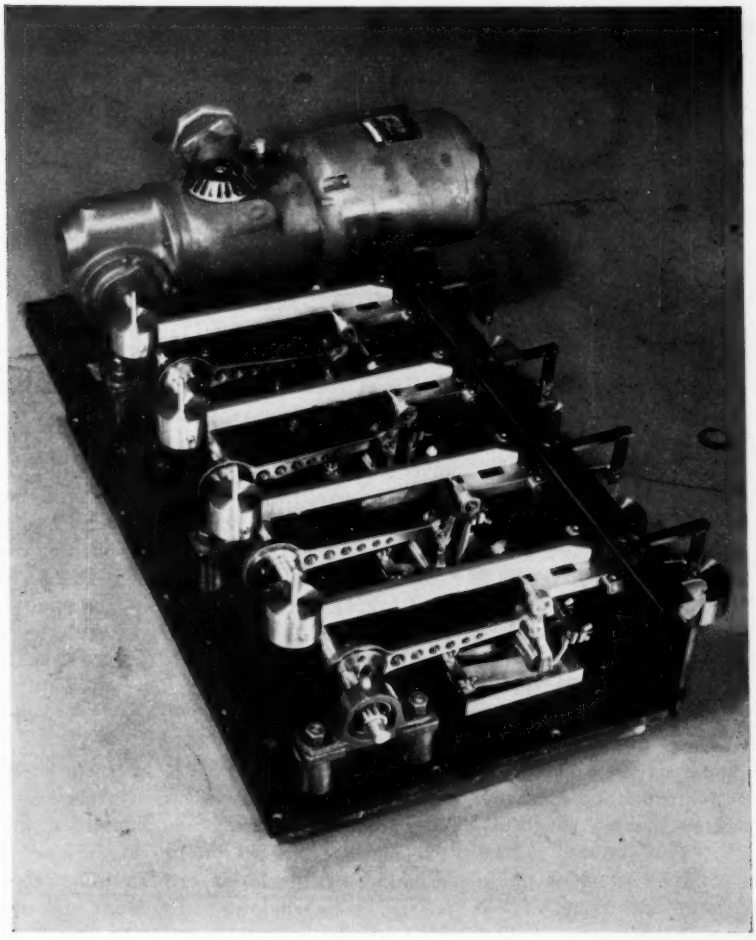


FIGURE 1.—Insole leather tester.

The specimen is supported on a brass block, A, 5 x 2.5 x 0.75 inches in size, with a curved depression 4 x 2.4 inches in area and approximately 0.4 inches deep at the lowest point (center) and curved to conform to the arc described by the roller, G. The leather test specimen, B, may be from 5 to 6 inches long and from 1 to 1.5 inches wide. The specimen is held at one end by a fixed clamp, C. and at the other end by a movable clamp, D. Slight tension is applied to the specimen by means of the 2.5 pound weight, E, which is

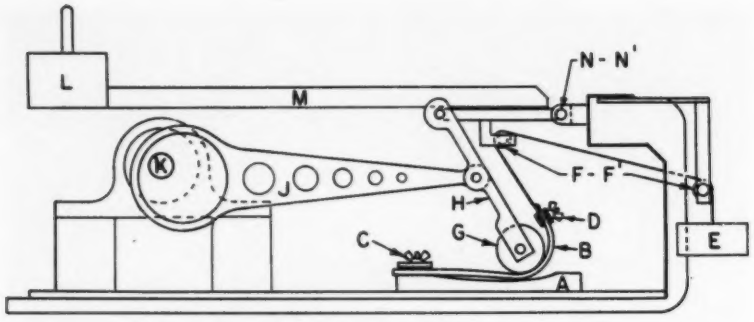


FIGURE 2.—Flexing mechanism of insole leather tester.

free to move vertically and which is attached to clamp, D, by a chain or a rawhide lace passing over small pulleys, F,F′. This tension causes the leather to flex around the brass roller G, which applies rolling pressure to the specimen. The roller is 1 inch in diameter, 1.5 inches long and is supported in the roller arm, H, by needle bearings. The roller arm and roller are driven by an eccentric and connecting rod, J. The stroke of the connecting rod is 1 inch and that of the roller is approximately 2 inches. Motion is supplied to the eccentric by the drive shaft, K, driven through a variable speed reducer so that the shaft speed can be varied from 15 to 125 revolutions per minute. Pressure is applied to the roller by the weight, L, acting through the lever arm, M, with fulcrum at the bearings, N,N′. The long arm is 12 and the short arm 3 inches long so that a weight of 1 pound at L applies a pressure of 4 pounds on the roller. A 1 pound weight, L, is shown in Figure 1 but additional weights can be added if desired.

The machine, excluding motor, is enclosed in a wooden case in order to maintain a uniform temperature and relative humidity around the specimens. The front and top panels of the case are made as one piece and hinged at the back. This "cover" can be lifted back so that the interior of the case is accessible for attaching specimens, adding sweat solution, or performing other necessary operations. There are large glass windows in the front and top panels of the cover.

A small, 3-inch fan circulates the air inside the case. A 600-watt, screw-type electric heater, connected through a variable transformer, permits hand temperature control to within a few degrees.

A counter mounted below the eccentric, J, and operated by a pin on J, records the number of times the specimen is flexed.

During a test the leather normally is kept damp, usually with water, artificial perspiration, or some modification of the perspiration formula. The solution can either be added at intervals from a pipette or equipment for adding it through the case can be installed if desired.

The machine is thus seen to be rather flexible. It is possible to vary the load on the specimen, the speed of flexing, the type of solution used for dampening the specimen, and the temperature. It is also possible, with some modifications to change the size of the roller.

In order to compare the pressure of a person on an insole with that of the roller on the specimen, some assumptions were necessary. It was assumed that the ball of a foot during a step covers about 5 square inches of the insole. The weight of a 200-pound person would, therefore, give a pressure of 40 pounds per square inch on the insole. The area of that part of the leather specimen which supports the load through the roller could only be estimated roughly. The length of this area was, of course, 1.5 inches. The width was assumed to be between $^1/_8$th and $^1/_{16}$th inches. A 4-pound load on the roller would, therefore, give a pressure of between 20 and 40 pounds per square inch on the leather. With a 1-pound weight at L, the pressure per unit area by the roller on a test specimen would then be roughly equivalent to that of a 100–200 pound person on his insole during walking. This was the standard weight used in testing with this machine.

Normally a rectangular specimen would be used for flexing on the machine, after which deterioration would be evaluated by tensile strength, stiffness or other measurements on test pieces cut from the specimen. During flexing, however, the specimen is distorted because of pressure, bending, and dampening. Tensile strength strips, for example, cut after machine flexing might, therefore, have quite different dimensions from those they would have had if cut before flexing. For comparative work, tensile strength specimens were cut as shown in Figure 3, before machine flexing. This was accomplished by putting a wooden block 3 inches wide under the middle of the 1 x 5 inch rectangular leather specimen, so that the die would cut only the narrow portion, B, (either ½ inch or 1 cm. wide) and shoulders of the test strip. Specimens cut in this manner behaved satisfactorily in the machine. After machine

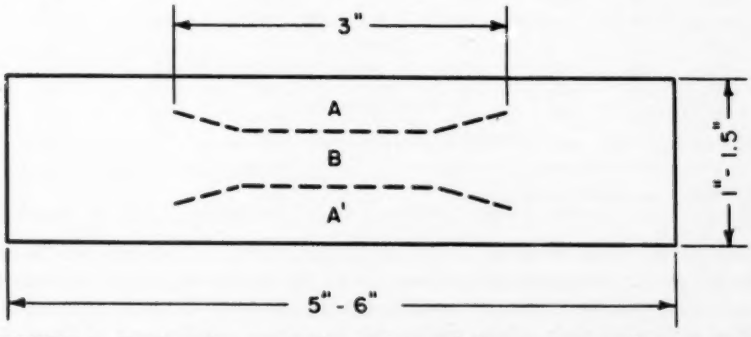


FIGURE 3.—Specimen for comparative work; permitting tensile strength measurement on either original dimensions or dimensions after machine flexing.

flexing, the side strips, A,A′, (Figure 3) were cut off and used for observations on stiffness, crackiness and other properties. The remainder was broken for strength. This method of precutting strength strips was useful for determining the effect of a given treatment or for comparing several treatments. Provided, of course, that the experiment was properly planned with comparable sets of strips correctly assigned, the strength either of treated and untreated strips or of strips with different treatments could be directly compared. Also, if desired, the strip dimensions could be measured before and after machine flexing, and tensile strengths calculated on either or both

TABLE I

Effect of Varying Machine Speed, Load and Time of Flexing on the Tensile Strength of Vegetable-Tanned Insole Leather

Load p. s. i.	Speed Cycles per min.	Cycles hundreds	Time Minutes	Tensile strength Block A Kg/cm²	Block B Kg/cm²	Block C Kg/cm²	Block D Kg/cm²
*	*	0	0	413	408	452	351
100	62	4	6	162	259	394	379
100	62	12	19	407	503	364	335
100	62	36	58	206	393	326	243
100	62	108	174	359	218	308	353
*	*	0	r	368	377	377	258
50	62	4	6	375	491	367	216
50	62	12	19	362	425	284	365
50	62	36	58	279	243	261	207
50	62	108	174	338	342	286	294
*	*	0	0	382	242	363	295
100	15	4	25	365	469	261	357
100	15	12	76	216	462	320	292
100	15	36	228	263	430	310	303
100	15	108	684	216	356	324	265
*	*	0	0	314	500	345	282
50	15	4	25	306	429	384	323
50	15	12	76	343	467	343	275
50	15	36	228	379	369	362	316
50	15	108	684	306	327	208	281
			Block Average	318	386	332	300

*Control, not flexed in machine.

bases by the usual method. Preliminaty data, shown in Tables I and II, on the effects of various machine adjustments on tensile strength of flexed specimens were obtained in continuous runs using comparable sets of specimens. After flexing on the machine the leather was dried, conditioned and tested. There were 4 replications or blocks. The artificial perspiration solution was

TABLE II

Average Tensile Strength Values (Rounded) for Different Machine Adjustments. (from data of Table I)

Cycles	Load* / Speed	100 / 62	50 / 62	100 / 15	50 / 15	Average
0		406	345	320	360	358
400		298	362	363	360	346
1200		402	359	322	357	360
3600		292	248	326	356	306
10800		310	315	290	280	299
Average		342	326	324	343	334

*Load in pounds per square inch; Speed in cylces per minute.

made according to the formula given in Federal Specification KK-L-311, with with 1 per cent of urea in addition.

Analysis of the data indicates that tensile strength was not influenced by the load on the roller or by the speed of flexing, but decreased somewhat as the number of flexes increased.

High tensile strength would not appear to be an important requirement for insole leather, therefore other tests for measuring insole deterioration were sought. No better method, however, has yet been found. This apparently agrees with the findings of Kremen, who uses tensile strength for his evaluation of insole leather deterioration. Measurement of stiffness of the flexed tensile strength strips before breaking was considered. Machine flexing, however, tended to decrease stiffness, therefore, this type of measurement does not seem suitable for evaluating the results of this test.

Acknowledgment

Acknowledgment is made to Mr. R. R. Calhoun, who built the machine and assisted in designing it.

References

1. Kremen, S. S. Evaluation and Improvement of Leather Insoles. Shoe and Leather Reporter, 265, No. 7, 15 (1952).

2. Maeser, M. A.L.C.A. Physical Testing Committee Reports, 1946–48; *J.A.L.C.A.*, **48** 197 (1953).

3. Beebe, C. W., Happich, W. F., Kip, W. S., and Rogers, J. S. Alum Retannage of Vegetable-Tanned Insoles Improves Their Serviceability. *J.A.L.C.A.*, **49**, 630 (1954).

Received, March 12, 1954.

Alum Retannage of Vegetable-Tanned Insoles Improves Their Serviceability*

C. W. Beebe, W. F. Happich, W. S. Kip and J. S. Rogers

United States Department of Agriculture
Agricultural Research Service
Eastern Utilization Research Branch
Philadelphia 18, Pennsylvania

It has been shown in previous work [1], [2], [3], [4], [5] that alum retannage imparts valuable properties to vegetable-tanned leather. There is an increase in resistance to acid deterioration, to moist heat, to molds and an increase in area stability. This type of retannage was first used to give increased durability to leather of the bookbinding and upholstery types. Its use was later extended to insole leather for shoes. In tests made at Camp Lee by the Quartermaster Board of the Armed Services, it was found that the use of alum-retanned insoles in place of vegetable-tanned insoles reduced the number of failures in the normal wear test by 68 per cent. W. Grassman and P. Stadler [6] have examined the effect of alkaline perspiration solutions on insole leather. They report a "good perspiration resistance of leathers which have been treated with cationic tannins and favorable conditions with regard to shriveling of samples retanned with chromium and alum salts". Work by this Laboratory has demonstrated that the optimum concentration of Al_2O_3 required to give maximum protection with minimum changes in the desirable characteristics of the leather is from 2.5 to 3.0 per cent on a moisture-free leather basis. It has been shown that the penetration of an aluminum sulfate tanning liquor could be increased by the addition of sodium acetate as a "masking" or "stabilizing" agent. Later, it was found that this mixture of aluminum sulfate and sodium acetate could be conveniently replaced by basic aluminum acetate, and in tannery operation the retannage could be effected by the addition of aluminum acetate to the other materials usually drummed into the leather in the tanner's oil wheel. The retannage can also be carried out by a "dry dipping" method in which the dry leather is dipped into a solution of basic aluminum acetate, in which the concentration, temperature and time of immersion are so regulated that the leather will pick up the required amount of Al_2O_3.

The Camp Lee test gave definite evidence that alum-retanned insoles were superior to vegetable-tanned insoles in actual wear. The recent "Mailmen's" service test [7], conducted by this Laboratory to study the serviceability of canaigre-tanned outsoles, afforded also an excellent opportunity to confirm the results of the Camp Lee test on the relative serviceability of vegetable-tanned and alum-retanned insoles.

This paper reports results obtained when control vegetable-tanned and alum-retanned leathers, prepared as described below, were tested as insoles

* Presented at the Fiftieth Annual Meeting at Bedford Springs, Penna., June 7, 1954.

in shoes in which the serviceability of outsoles was being simultaneously studied.

Preparation of Test Leathers

Through the cooperation of the Middleburg Tanning Corporation, the alum retannage was carried out at their tannery at Middleburg, Pennsylvania. From regular vegetable-tanned bellies suitable for insoles, 3 lots of 15 bellies each were retanned by the "dry dip" method to contain approximately 2.5, 2.75, and 3.00 per cent Al_2O_3. Three lots of 50 bellies each were retanned by the oil wheel method to give leathers with approximately 2.75 per cent Al_2O_3. Except for minor variations, these bellies were all finished by the normal tannery procedure. Pieces of the leathers taken immediately after retanning contained the desired concentrations of Al_2O_3. However, when the leathers were finished, the concentration of Al_2O_3 in the outer layers had decreased considerably. This was attributed to subjecting the rough, dry leather to the action of a "sour dip" (a fermenting mixture of glucose and Epsom salts) for a rather long period. This removed from the outer layers some of the alum before it was firmly fixed. The alum was restored to the outer layers by dry dipping in an aluminum acetate solution of the required strength. When finished and dried, these alum-retanned insole leathers were entirely free from any indication of cracky grain.

To furnish leather for the control insoles, 16 vegetable-tanned bellies, not retanned, but in other respects as similar as possible to those used for retanning, were selected. From the center of each belly 5 to 7 insoles were cut. Each retanned insole was matched with a control vegetable-tanned insole of the same thickness and cut from the same location on the belly. Each pair of insoles was then used in the preparation of a pair of test shoes.

Wear Test

In the actual service test 61 pairs of shoes were worn until the original outsole and 2 resoles had been worn through. The periods of wear ranged from 9 to 12 months. When the second resoles were worn through examination of the insoles indicated that the test had progressed to such a stage that the relative serviceability of the vegetable and alum-retanned insoles could be evaluated. The wear test was then discontinued and the condition of the worn insole leathers compared.

Chemical Analysis of Test Leathers

Analyses of the original leathers before use and of the worn insole leathers are shown in Table I [8]. The analysis of the vegetable-tanned control leather was made on a sample composited from the belly leathers used. The analysis of the alum-retanned leather is a calculated average of the analyses of 12 separate bellies. The Al_2O_3 content ranged from 1.9 per cent to 3.8 per cent,

TABLE I

Analysis of Leathers Before and After Mailmen Service Test
(Results on Moisture-Free Basis)

		Before Test		After Test	
		Vegetable Control	Alum Retan	Vegetable Control	Alum Retan
Petroleum Ether Extract	%	6.6	5.0	8.2	7.2
Insoluble Ash	%	0.3	2.5	0.8	2.9
Hide Substance	%	30.5	31.0	41.8	40.0
Soluble Matter	%	39.7	28.1	28.5	18.0
Combined Tannin	%	22.9	33.4	20.7	31.9
Degree of Tannage	%	75.1	107.7	49.5	79.8
Soluble Nontannin	%	27.3	23.9	12.7	12.2
Soluble Tannin	%	12.4	4.2	15.9	5.8
Total Ash	%	9.4	8.0	4.7	6.0
Total Al_2O_3	%	——	2.8	——	2.5
Total Al_2O_3 on hide substance basis	%	——	9.0	——	6.3
pH*		3.1	4.1	5.1	5.1
Shrink Temperature, C°*		83.5	107.	82.	99.

*Not on moisture-free basis.

but of the 70 insoles cut from the bellies 60 had Al_2O_3 contents ranging from 2.4 per cent to 3.0 per cent, 5 contained 1.9 per cent and 5 contained 3.8 per cent.

Physical Tests and Evaluation of Leathers

Representative samples of the original control and alum-retanned leathers were evaluated for their resistance to perspiration and repeated flexing and drying by use of an insole testing apparatus[9]. This tester was designed to flex the leather while moistened with a synthetic sweat solution to hasten the deterioration and approximate, as nearly as possible in a laboratory test, actual wearing conditions. The conditions and specimens used in conducting this test were as follows:

Test specimen .....1 inch by 5 inches[9]
(with a dumbell specimen cut but adhering at its ends to the test specimen)
Temperature .....100° F. (38° C.)
Speed .....60 cycles per minute
Tension .....2.6 lbs.
Load on roller .....about 4.0 lbs.

The synthetic perspiration solution was prepared by the method described in Federal Specification KK-L-311a[10] as modified by Kremen[11] and has the following composition:

For one liter of solution use:

NaCl	10 grams	
$(NH_4)_2CO_3$	4 "	
Na_2HPO_4	1 "	
Urea	240 "	(approximately 4 molar)

Adjust to pH 7.8 with lactic acid, then dilute to volume with distilled water.

The procedure was as follows: The thickness of each dumbbell specimen was determined and recorded. The specimens were then placed in the tester and

(1) Flexed 5 minutes dry at 60 cycles per minute (300 cycles).
(2) Three ml. sweat solution added while running and flexed for 30 minutes, equal to 1800 cycles.
(3) Two ml. sweat solution added while running and flexed for 120 minutes, equal to 7200 cycles.
(Total number of cylces—9300).

The specimens were removed from the tester and placed in an oven at 39–41° C. for one hour, and then conditioned at 23° C. and 50 per cent relative humidity overnight. This entire treatment was repeated on 2 suc-

TABLE II

Tensile Strength of Vegetable and Alum-Retanned Leathers Before and After Testing on EURB Insole Tester

Belly No.	Vegetable Control			Alum Retan		
	Before Kg/Cm²	After Kg/Cm²	Loss %	Before Kg/Cm²	After Kg/Cm²	Loss %
1	130	86		128	112	
2	173	68		161	143	
3	194	85		208	164	
4	198	84		211	126	
5	228	108		227	135	
6	230	56		231	178	
7	231	89		231	170	
8	239	39		232	180	
9	244	68		239	110	
10	250	109		263	161	
11	265	82		289	162	
12	269	97		305	154	
13	290	86		320	197	
Average	226	81	64	234	153	35

Strength remaining after test as % of original strength—Control 36
Strength remaining after test as % of original strength—Alum 65
Improvement by alum retannage $\frac{65-36}{36} \times 100$ 81

sessive days. The dumbbell specimens were then cut loose from the large specimens and tested for tensile strength (See Table II) and for crackiness by bending around standard diameter mandrels as described in the A.L.C.A. Official Methods [8]. The results of the cracking test and the diameters of the various mandrels used are shown in Table III and Figure No. 1.

TABLE III

Crackiness of Vegetable and Alum-Retanned Leathers, by Mandrel Method. Before and After Testing on EURB Insole Tester

(Reported as diameters of mandrels required to produce cracks)

Leather No.	Vegetable Leathers		Alum-Retanned Leathers	
	Before Diam. Inches	After Diam. Inches	Before Diam. Inches	After Diam. Inches
1	0.45	2.00	0.45	1.63
2	0.38	2.00	0.38	1.50
3	0.38	2.00	0.38	1.25
4	0.31	2.00	0.31	1.13
5	0.31	2.00	0.25	1.00
6	0.25	2.00	0.25	1.00
7	0.19	1.88	0.19	0.88
8	0.19	1.39	0.13	0.88
9	0.19	1.00	0.13	0.88
10	0.19	0.88	0.13	0.75
11	0.13	0.88	0.13	0.56
12	0.13	0.75	0.13	0.50
13	0.13	0.75	0.13	0.31

The worn insoles were further evaluated and sorted for quality by inspection for crackiness, curling, discoloration and deformation. They were graded on a scale ranging from 0, the poorest, to 10, equal to the unworn leather. Ratings were made separately by four sorters and were highly uniform between individuals, None of the worn insoles were rated higher than six on the scale. The results of the ratings are shown in Table IV. It was the opinion of a shoe repairer that shoes containing insoles with ratings of 0 to 2 were unsuitable for repair and further use; while those rated 3 or above could still be used. Figure 2 shows the relative percentages of worn vegetable-tanned and alum-retanned insoles that were of quality that would justify resoling the shoes for further wear.

Breaking strength determinations were made on the original leathers and on the worn insoles. The breaking strength of the original leathers is the average of 15 determinations of fairly close agreement. Since the condition of the worn insoles did not permit strength determinations on every insole, determinations were made on several insoles from each rating as described above. The breaking strength apparently was in harmony with the rating

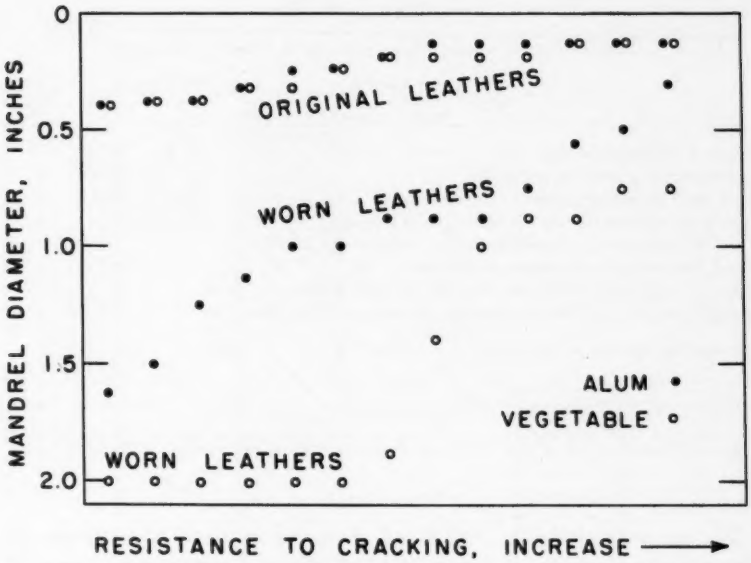


FIGURE 1.—Mandrel diameters at which original and worn leathers cracked on bending.

TABLE IV

Rating of Worn Insoles by Inspection

Rating Scale	Number of Insoles						
	0	1	2	3	4	5	6
Alum Retan	0	2	7	21	16	11	4
Vegetable	1	12	18	18	8	2	2

Soles suitable for repairing, 3 and above, Alum	—52	85%
Soles suitable for repairing, 3 and above, Vegetable	—30	49%
Improvement by alum retannage $\frac{85-49}{49} \times 100$		73%

given and was independent of the type of tannage, therefore, data from both tannages were combined to give the averages shown in Table V. The leathers in classes 0 and 1 were so badly deteriorated that samples often broke while being fastened in the strength tester and determination of breaking strengths was impossible. For this reason the arbitrary figure of 5 kilograms strength which has been used for this class is simply an estimated value. The figures in the second part of Table V are calculated from data in the first part of the table.

TABLE V

Deterioration of Insoles Based on Loss in Breaking Strength*

	Original Leathers			Worn Insoles			
	Vegetable	Alum Retan	Average	Classes 4, 5 & 6	Class 3	Class 2	Classes 1 & O
Breaking Strength in Kg.	92	96	94	70.5	58.2	29.6	5.**
Deterioration (loss in strength) %				25	38	69	95.
% of total vegetable insoles in various classes				19.7	29.5	29.5	21.3
% of total alum-retanned insoles in various classes				52.4	32.8	11.5	3.3
Total deterioration of vegetable-tanned insoles—%				57			
Total deterioration of alum-retanned insoles—%				37			
Strength remaining (100-Deterioration) vegetable insoles				% 43			
Strength remaining (100-Deterioration) alum-retanned insoles				% 63			
Improvement by alum retannage $\frac{63-43}{43} \times 100$				% 47			

*Since thickness measurements on worn insoles are not directly comparable with those made on the original leathers, breaking strength data instead of tensile strength data have been used.

**Since the condition of insoles in 1 and 0 classes was such that samples broke when being put in strength tester, an estimated average value of 5 kg. was used on these classes of worn insoles.

Discussion

The analyses of leather in Table I show the effects of alum retannage. The amount of combined tannin and the degree of tannage are increased; there is a corresponding decrease in the amount of soluble matter and soluble tannin. During wear the insoles have picked up a slight amount of oil and insoluble ash. There has been a decrease in soluble matter. In spite of this there has been a slight increase in the amount of soluble tannin and a decrease in the degree of tannage. This may indicate that wear has resulted in some detannage. If this detannage has some deleterious effect on the wear of the leather, the higher degree of tannage of the alum-retanned leather as compared with that of the vegetable-tanned leather would be beneficial.

According to the ratings in Table IV the alum-retanned insoles stood up in service much better than the vegetable-tanned insoles. Out of 61 insoles, 52 were included in ratings 3 to 6 thus showing greater resistance to service. In the case of the vegetable-tanned insoles only 30 of the 61 insoles were placed in groups 3 to 6. In Table IV it will be noted that about 85 per cent of the alum-retanned insoles are still serviceable while only about 49 per cent of the vegetable-tanned insoles are still serviceable. On this basis the alum-retanned leathers are 73 per cent better than the vegetable-tanned leathers.

A comparison of the data given in the tables shows that in every case there is a decided improvement resulting from alum-retannage. The figure of 73 per cent improvement shown in Table IV is probably the most valid as this indicates in a practical way the value of the insoles after being worn. This figure does not correlate with the value of 47 per cent improvement as obtained by breaking strength measurements on the original and worn leathers,

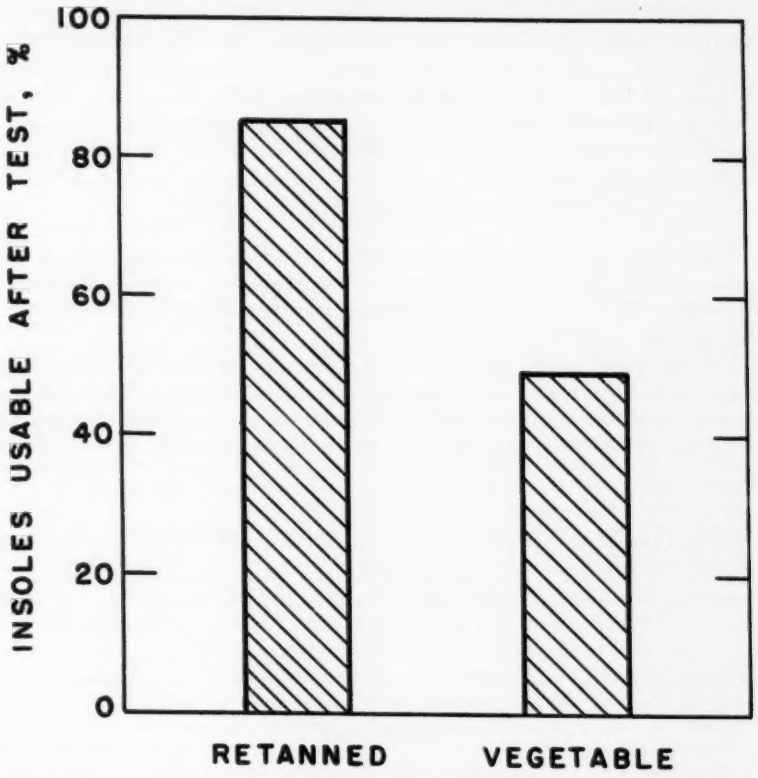


FIGURE 2.—Percentages of worn vegetable and alum-retanned insoles still serviceable after the test.

but does correlate quite well with the value of 81 per cent obtained with the insole testing machine based on tensile strength figures. The values for grain crackiness based on results obtained by bending specimens around mandrels of different diameters are not susceptible to simple mathematical comparison but Table III and Chart 1 show the superiority of alum-retanned leather to the vegetable-tanned leather.

It was mentioned that 5 alum-retanned insoles had considerably more Al_2O_3 than the average and that 5 had considerably less. It was hoped that these tests would give some further indication of the optimum amount of Al_2O_3 which should be present. However, it was found in each case that the number of samples was insufficient to rule out discrepancies due to the individual wear.

The wearers of the test shoes, in general, found them very comfortable. The only cases of discomfort were those usually attending the breaking in of new shoes and these were evenly divided between the two types of leather. Toward the end of the test, insoles which were badly cracked or deformed were uncomfortable irrespective of the tannage. There were no cases of discomfort reported that could be attributed directly to the use of alum-retanned insoles.

Conclusions

This series of tests demonstrates that the alum retannage process for making insole leather can be successfully applied in a commercial tannery to produce a satisfactory alum-retanned leather having an Al_2O_3 content ranging from 2.5 to 3.0 per cent.

The results of actual service tests in shoes and of laboratory testing of vegetable-tanned and alum-retanned insole leathers show that alum retannage increases the serviceability of insoles about 70 per cent and results in no noticeable deleterious effects on the wearer of the shoes.

Acknowledgments

We acknowledge with thanks the cooperation of the Middleburg Tanning Corporation in alum-retanning the insole leathers, of the International Shoe Company in making the experimental shoes, and of the officials and mail carriers of the Chestnut Hill and Germantown Stations of the Philadelphia Post Office and of the Glenside and Hatboro Post Offices in conducting the service tests on the experimental shoes.

References

1. The Permanence to Acid Deterioration of Vegetable Leather Retanned with Alum. R. W. Frey and C. W. Beebe. *J. Amer. Leather Chemists Assoc.*, **35**, 440 (1940).
2. Accelerated Aging Tests on Alum-Retanned Vegetable Leathers. C. W. Beebe and R. W. Frey. *J. Amer. Leather Chemists Association*, **37**, 539 (1942).
3. Physical Properties of Alum-Retanned Vegetable Leathers. C. W. Beebe and R. W. Frey. *J. Amer. Leather Chemists Association*, **37**, 478 (1942).
4. Quartermaster Board Project T-362. Report of Test of Boots, Service, Combat, with Experimental Insoles. QMB T-1432, March 3, 1945.
5. Private Communication to G. Arthur Brown, Leather Technologist, Army Service Forces, Office of the Quartermaster General, April 24, 1946.
6. Die Schrumpfung der Brandsohlen unter Schweisseinwirkung. (The Shriveling of Insole Leather Under the Action of Perspiration.) W. Grassmann and P. Stadler. *Das Leder*, **4**, 218, October, 1953.
7. Canaigre Root Tannin Serviceable Leather. C. W. Beebe, W. S. Kip, W. F. Happich and J. S. Rogers. J. Amer. Leather Chemists Assoc., **49**, 228 (1954).
8. *A.L.C.A.* Methods of Sampling and Analysis.
9. Insole Leather Tester. I. D. Clarke and R. M. Flaherty. *J. Amer. Leather Chemists Assoc.* **49**, 585, (1954).
10. Federal Specification KK-L-311a, Method 3211, January 19, 1953.

11. Private Communication from S. S. Kremen of Tanners' Council Research Laboratory, dated October 5, 1949.

Received March 12, 1954.

ABSTRACTS

Filter Method for the Quantitative Analysis of Tanning Materials. Anon. *Das Leder* **5,** 28 (1954). A revision of the filter method for the determination of tannin, is presented for discussion. I. D. C.

Leather Making in Antiquity and its Preservation. By A. Gansser-Burckhardt. *Das Leder* **5,** 83 (1954). One method for restoring historical leather objects is treatment with glycerin or linseed oil, often without sufficient preliminary cleaning. Linseed oil must be avoided, if the leather is to be examined further. The authors' method is to remove as much foreign matter as possible, then to oxidize putrescible, organic matter by oxidation with permanganate followed by treatment with sodium bisulfite to reduce excess permanganate. If the leather is very fragile, foreign matter is removed by treating the object first with a solution of sodium bicarbonate, then, without washing, with dilute hydrochloric acid. The evolved carbon dioxide removes dirt. Curled or twisted, brittle leather pieces are treated with warm, moist air at 40°C until they can be cleaned as above. The tannin has changed so that little soluble matter is lost during the above treatmenst. Determining the nature of the leather is a difficult problem. The grain is often destroyed so that the type of hide can not be determined, unless a hair can be found. The tannin does not give the normal color reactions. Paper chromatography offers some promise. I. D. C.

The Durability of Upholstery Leather from Split Hides III. By G. P. Cachia, R. F. Innes and R. G. Mitton. *J. Soc. Leather Trades' Chemists,* **38,** 74 (1954). It has been previously demonstrated that atmospheric deterioration of vegetable tanned upholstery leather is greatly enhanced by the presence of ionic iron. Hence a study of possible treatments to prevent this action was indicated. To leather samples of dressing hides from three tanneries, additions were made of the following salts: (a) none, leather as received; (b) sodium pyrophosphate; (c) calcium pyrophosphate; (d) sodium oxalate; (e) calcium oxalate; (f) alum. Half the samples were further treated with 1000 p.p.m. of iron. After exposure to an atmosphere polluted with oxides of sulfur in a gas chamber [J.S.L.T.C., 37, 158 (1953)], the samples were analyzed and tested by the buckle tear test and the lastometer. Chemical analyses and strength tests, as measures of degradation, gave good agreement; but the samples treated with calcium pyrophosphate, while best in the lastometer test, were weakest in the buckle tear test. The difference is shown to be due to the fact the calcium salt was precipitated on the outside of the leather, leaving the interior unprotected. This is likely to happen whenever an attempt is made to incorporate an insoluble salt in a leather by first introducing a soluble salt and then drumming in a solution which precipitates the insoluble salt. Sodium pyrophosphate gave complete protection in these experiments but did not prevent an increase of acid in the leather. This may have been due to SO_2 in the gas chamber atmosphere. Calcium pyrophosphate was equally good in protecting the layers it penetrated. Of the other salts, sodium oxalate was a poor second to the phosphates and was followed by alum, calcium oxalate and no salt (worst) in that order. The poor results obtained with calcium oxalate are not solely due to surface precipi-

tation. They are attributed to free oxalic acid. If this is correct it indicates the necessity of careful washing after the calcium oxalate treatment. Iron added to leather acts as a catalyst in the conversion of sulfur dioxide to sulfuric acid, consequently facilitating the rotting. The action of the extra iron added to some of the samples was apparently completely inhibited by sodium pyrophosphate and, to the extent to which it penetrated, by calcium pyrophosphate. Sodium oxalate greatly reduced the extra iron action and may be as effective as the phosphates although there is evidence that it is not. Calcium oxalate is certainly less effective if the iron is added, as in these experiments, after the precipitation of the oxalate. Alum appears not to affect the iron although it decreases the attack of the acid produced. It is suggested that leather may be protected against action by polluted atmosphere by the addition of two salts, the first chosen to inhibit the catalytic effect of the iron present, and the second chosen with the view to protection against strong acid taken up by the leather. Work is required to test this suggestion and determine the proportions in which the two salts should be added. In the meantime greatly increased protection can be gained by the incorporation of soluble pyrophosphates. R. H. T.

The Precursors of Red Color in Leather. By W. E. Hillis. *J. Soc. Leather Trades' Chemists*, **38,** 91 (1954). The bark and wood of certain Eucalyptus species are capable of supplying large quantities of tannin but are restricted in use because of imparting red color to leather and marked astringency. A previously reported method for producing color quantitatively developed from the leuco-anthocyanins was used in this study. The term "leuco-anthocyanins" denotes that class of substances which, when heated with dilute HCl, particularly in alcoholic medium, gives the brilliant color of anthocyanidin. The anthocyanidins produced by the Eucalypt tannins studied after heating with HCl and propanol were found to be: mallet bark 13.1 and 12.2; red iron bark, inner bark 4.0, intermediate bark 10.0 outer bark 9.9 per cent delphinidin; "Myrtan" extract 5.8 and red stringy bark inner bark 2.8 per cent pelargonidin. No anthocyanidins were produced by myrobalams extract and 4.9 per cent delphinidin by wattle extract. It is suggested that the leuco-anthocyanins, from which the anthocyanidins originated, are the precursors of the red color in leather. Attempts to improve the yield of cyanidin from Butea frondosa kino were unsuccessful. The leuco-anthocyanins in the bark of radiata pine yielded 9.9 per cent of cyanidin and may be responsible for the instability of the tannins in this bark. R. H. T.

A Comparison of Methods of Determining the Percentage Basicity of One Bath Chrome Liquors. D. Burton and M. Thompson. *J. Soc. Leather Trades' Chemists*, **38,** 102 (1954). A comparison is made of three methods for determining the percentage basicity of one bath chrome liquors. The methods compared are the Lehigh Method [*This Jour.*, **47,** 588 (1952)], the Procter-McCandlish Method [*Soc. Leather Trades' Chemists. Official Methods of Analysis*, 116 (1951)] and the Burton-Glover-Wood Method [*J.S.L.T.C.*, **25,** 103 (1941)]. The results obtained are tabulated. Conclusions from the results are as follows: An erroneously high value for the percentage of basicity is given by the Procter-McCandlish Method in all cases where anions have entered the chromium complex to an appreciable extent. The Burton-Glover-Wood Method gives satisfactory results with straight chrome liquors. It is, however, not applicable in the cases of liquors containing masking salts which are oxidizable by hydrogen peroxide giving carbon dioxide. This acid is expelled on acidification resulting in a high result for the basicity obtained. The Lehigh Method gives satisfactory results with all the solutions. Owing to the small titration figure (found by difference) the error of one drop gives a much larger discrepancy in the results

than a similar error would give with the other methods. Thus, for research purposes, a finely calibrated burette and a pH meter are necessary. The Burton-Glover-Wood Method is preferable to the Lehigh Method for "straight" chrome liquors because a class "B" burette and indicator (phenolphthalein) give an accuracy of an order which is only obtainable with the latter when a semimicro burette (10 ml.) and a pH meter are used.—R.H.T.

The Molecular Weight of Black Wattle Tannins. I.—The Application and Standardization of Apparatus for Accurate Measurements. S. R. Evelyn. *J. Soc. Lea. Trades' Chemists*, **38**, 142 (1954). A study was made of the use of the Ray ebulliometer [*Trans. Faraday Soc.*, **48**, 809 (1952)]. Modifications for improving the instrument are described. The accuracy of the instrument was checked by determination of the molecular weight of penta-ethyl-d-catechin. A mean value of 491 ± 5 was found as against the calculated value of 500.4. High reproductibility was obtained. The ebulliometric measurements were compared with results obtained with cryoscopic measurements carried out in bromoform. Determinations were made on methylated and acetylated tannins and the actual molecular weights of the original tannin calculated as follows: Acetylated materials:

$$\text{Molecular wt. original} = \text{mol. wt. found} \times \frac{1}{100}\,(100 - \text{acetyl value} \times \frac{42}{43}).$$

Methylated materials.

$$\text{Mol. wt. original} = \text{mol. wt. found} \times \frac{1}{100}(100 - \text{methyl value} \times \frac{14}{31}).$$

Molecular weights calculated from the ebulliometer results are: Acetylated sample 1083 ± 22: Methylated sample 1271 ± 35. Subsequent work indicated that the difference is due to the elimination of nontan sugars and gums during methylation and the inclusion of these impurities in the product obtained by acetylation. R. H. T.

Chromatographic and Electrophoretic Testing of Dye Mixtures. By W. Grassman and L. Hübner. *Das Leder* **5**, 49 (1954). A review is given of chromatographic methods, both one and two dimensional, and of electrophoretic methods for separation of mixtures. Chromatographic separations may be made with water or with organic solvents. If a round filter paper is used, rings of various components are formed around the point where the dye was applied. Bands are formed if a paper strip is used. Electrophoresis may be used on a paper strip to separate ions. By blowing a little of the dye onto moist filter paper, specks of different color will appear, if the dye is a mixture. The result of an examination of 6 acid dyes is reported; colored plates are given to show the types of chromatographs obtained. Basic dyes are firmly fixed by cellulose in water, but chromatographic separations can be obtained with water-alcohol, water-butanol, collidine or acetic acid. Electrophoretic separations are best made in 6 per cent or 50 per cent acetic acid. Continuous electrophoresis can be used to determine whether an acid and a basic dye form loose addition compounds when they do not precipitate. If spots of each dye are placed on paper a short distance apart, then current is applied and solvent is allowed to flow downward, the streaks that form will cross in a sharp line if there is no reaction. If the two form a compound, there will be a change in direction and a diffuse zone where the two streaks meet, after which they continue in their original directions. For quantitative analysis, strip chromatographs may be read with an apparatus consisting of a light source and slit on one side of the paper and a photocell on the other. Standard curves with known quantities of dye are then required. I. D. C.

The Theory of Leather Dyeing VI. A Study of the Combining Reactions Between Aromatic Substances and Proteins. By Gerhard Otto. *Das Leder* **5**, 61 (1954). The formation of dipoles results in increased electron mobility. This mobility is found in systems of conjugated double bonds and is greater the longer the system. Dyes often have long systems. Siriuslichtgelb RT has a chain of 17 conjugated double bonds. It has a great affinity for leather and therefore does not penetrate well. There is a widespread belief that penetration of a dye is a function of molecular size, and is less the greater the size. This is not true; penetration depends rather on gross dissociation. Some dyes do not follow this rule, but examination of their structure shows that the conjugate double bond system is broken by an isolating group so that the electron cloud can not oscillate over the whole molecule but only in two shorter paths. Isolating groups may be $-CH_2-$, $-O-$, $-NH-$, $-S-$, or meta substitution in the ring instead of para. The greater electron mobility that results in chromophoric activity is also the cause of the coordinate affinity between the dye and fiber. Mobile electrons cause formation of dipoles and favor the formation of hydrogen bridges. Isolating groups in the dye therefore would lower the affinity between dye and fiber and increase dye penetration. This effect was shown by tests with the following 3 dyes: Siriuslichtbraun RL (molecular weight, 687), Säurelederbraun EGB (mol. wt. 703) and Diaminechtbraun GB (mol. wt. 896). The first dye has a system of 11 conjugate double bonds, the second has 2 systems of 6 conjugate double bonds, separated by a meta substitution in one of the benzene rings, and the third has an NH isolating group, separating a system of 5 from one of 8 conjugate double bonds. All have approximately the same gross dissociation, as is shown by the fact that all have solubility limits at pH 1.3-1.4. (The lowest Ph value at which an anionic dye is completely soluble is an approximate measure of its gross dissociation). The dyes were washed through columns of hide fibers and of filter paper as follows: The column (10 mm. diameter) was first washed with buffer solution at pH 4.5, a pH value typical of mildly neutralized chrome leather; then 10 cc. of a 0.02 molar solution of electrolyte-free dye and finally 50 cc. of dye-free buffer solution were sucked through the column. The lengths of dyed hide in the columns were 22, 63 and 58 respectively for the 3 dyes in the order given above. The corresponding lengths for the paper columns were 19, 81 and 30. The relative penetrations into chrome leather were 2, 5 and 5 respectively. The dye with an uninterrupted system of 11 conjugated double bonds thus had the greatest affinity for hide and penetrated least. I. D. C.

The Formation of Simple, Masked Chromium Complexes. VII. The Constitution of Chromium Complexes with Dicarboxylic Acid Radicals. By A. Küntzel, H. Erdmann, H. Spahrkäs and O. Mischitz. *Das Leder* **5**, 73 (1954). This and the preceding article [*This Jour.* 49, 118] are concerned with the maximum number of acid radicals that can enter the chrome complex. From these data and the stability of these complexes on aging conclusions regarding their constitution are possible. When 3 mols (per chromium atom) of the various masking salts were added to 0% basic chromium chloride solutions containing 0.1% chromium, conductivity dropped for 1-2 hours, then was nearly constant. Conductivity was less the greater the molecular weight of the masking salt. Maximum take up of acid radicals was found, as in previous work, by diluting the chrome solution 200 fold, then titrating at once with N/200 hydrochloric acid. The titration curves were compared with curves obtained by titrating known amounts of pure masking salt. In previous work there was no self buffering by the complexes, because these were either cationic or uncharged complexes or, if anionic, were strongly dissociated. The titration curves of the chrome solutions with excess masking salt therefore had the same character as those for the pure masking salt. This was not true for the complexes with dicarboxylic acids. If

both carboxyl groups were weakly dissociated, the complex had decided buffering action and the curves differed from the comparison curves. The maximum take-up could not be determined except when there was only a slight excess of masking salt present in the chromium solution. The curves for malonic acid (dissociation constants: K_1, 1.42×10^{-3}; K_2, 2.03×10^{-6}) did not follow exactly any of the curves for pure malonate, but it was evident that practically a maximum of 6 equivalents (3 mols) of malonate were bound coordinately by a chromium atom. This blue-violet complex was very stable as it did not change to green on long aging as did the oxalate complex. Malonate forms a 6 membered ring with chromium and this is more stable than a 5 membered ring such as is formed by oxalate; the rings are the same except that the malonate ring has a CH_2 group between the two carbon atoms. (See this Jour. 49, 119, Fig. VI). On addition of 1, 2, 3 or 8 equivalents of sodium succinate (K_1, 6.4×10^{-5}; K_2, 3.3×10^{-6} for the acid) to 0% basic chromium chloride (0.1% Cr) the solution remained clear. With 4 equivalents precipitation started in 1 hour and was complete in 8 days. With 5 and 6 equivalents precipitation started in 6 hours and 14 days respectively. On heating in sealed tubes for 5 minutes at 100°, solutions with 1, 2, 6 and 8 equivalents of succinate remained clear, but those with 3, 4 or 5 equivalents contained a flocculent precipitate that indicated decomposition of the complex to chromium hydroxide and succinic acid. The precipitate with 4 equivalents of succinate was dried a 50° under high vacuum then analyzed for chromium, carbon and hydrogen. The calculated ratio of chromium to succinate to excess hydrogen was 1:1.00:4.23 so that the precipitate probably consists of a network of chromium atoms joined by succinate radicals in one direction and by hydroxyl groups in the other. Two chromium atoms are joined by a succinate radical through two 5-membered rings involving carboxyl and coordinately bound water as was found for acetate (This Jour. 46, 118, Fig. II). The titration curves indicated 1.5 to 2 succinate radicals per chromium atom, but there was considerable self buffering so that a trisuccinate complex is not ruled out. By chelation a 7 membered ring would be formed and this would be comparable in stability to a 5 membered ring. Maleic acid (K_1, 1.42×10^{-2}; K_2, 8.57×10^{-7}), when added as the sodium salt to chromium chloride solutions, caused a color change to yellowish green and a slight turbidity that redissolved in 1 day or less. After 24 hours the solutions were blue. Heating in a sealed tube caused a precipitate only with 5 equivalents of maleate. Titration indicated a complex with 2 or 3 residues. Chelation would result in 7 membered succinate rings with 2 double bonds; these would be less stable than the 7 membered succinate ring. Fumaric acid (K_1, 9.50×10^{-4}; K_2, 4.80×10^{-5}) is isomeric with maleic acid but because of steric hindrance can not form chelate compounds. It forms precipitates if 2 or more equivalents are present. The ratio of chrome to fumarate radicals to excess hydrogen in the precipitate was 1 : 1.06 : 2.58. This indicates long chains of chromium atoms joined by a fumaric acid radical. Adipic acid (K_1, 3.7×10^{-5}, K_2, 2.4×10^{-6}) was similar in behavior to succinic acid, but if 3 or more equivalents were added, precipitates formed. The precipitate had the same structural composition as that with succinic acid. Phthalic acid (K_1, 1.0×10^{-3}; K_2, 4.7×10^{-6}) was also quite similar in masking action to succinic acid. Clear solutions were obtained when 1, 2, 6 and 8 equivalents of sodium phthalate were added to 0 basic chromium chloride solutions. With 3, 4 and 5 equivalents turbid solutions were formed after several days or a month. Precipitates were formed only in small amounts because of the stronger dissociation of phthalic acid. Chelate compounds had 7 membered rings. Sulfophthalic acid behaved essentially the same as phthalic with the exception that it did not form precipitates because of its greater acidity. In summary, the chrome solutions masked with all of the dicarboxylic acid radicals, except sulfophthalic, became turbid, especially in the range of from 3 to 5 equivalents of masking salt per chromium atom. On aging, especially with the higher amounts of masking salt, the precipitates redissolved, except for those with fumarate and adipate. Formation of a precipitate is caused by a

chain like coupling of dicarboxylic acid radicals and chromium atoms with one chromium atom per carboxy group. Solution of the precipitate is connected with decomposition of the chain network and formation of rings on a single chromium atom. These rings may be 5, 6 or 7 membered depending on the acid. Each chromium can accommodate 3 rings and therefore 3 mols or 6 equivalents of a dicarboxylic acid. The sulfo groups of sulfophthalic acid do not enter into ring formation. Precipitates which do not redissolve are formed if ring formation is prevented by steric hindrance (fumaric acid), or if the ring would have too many members (as 9 for adipic acid). Precipitates which form on long aging (oxalic, maleic) are stable, high molecular, aggregates containing hydroxyl groups. Stability of the acidochrome complexes increases with number of members in the ring from 7 to 5 to 6. The 6 membered ring of malonatochrome complex is so stable that it does not change to acidohydroxochrome complex even on aging for years. I. D. C.

XXIII

BALANCED PERFORMANCE

...and with NOPCOLENES that means surface lubrication with controlled penetration

In mountain climbing, perfect balance and coordinated action, sure penetration of piton and axe in ice or rock, can mean the margin between a successful step upward or a perilous plunge downward.

In fatliquoring leather, as in mountain climbing, *balanced* performance—effective *dual action*—is vital. That's why the new, *double-action* Nopcolene* fatliquors are so important to your leather processing.

These specially developed products give excellent surface lubrication plus controlled penetration—a balanced performance that results in tight grain, good tensile strength and stitch tear, at the same time permitting the tanner to achieve whatever degree of temper, softness, hand, break or stretch desired.

Nopcolene fatliquors are readily soluble. Since many of them are moisture-free, others containing not more than 6-7% moisture, you save on freight, handling and storage.

Unless you are already using Nopcolenes, try them for leather products that can mean greater profit and prestige for you. Send today for full details.

***FREE!** This book gives up-to-the-minute data about Nopco's Nopcolene* fatliquors and formulas for various leathers. Write for a copy.*

*T. M. Reg. U. S. Pat. Off.

NOPCO

Chemical Company, Harrison, N. J.

Branches: Boston • Chicago • Cedartown, Ga. • Richmond, Calif.

Sterozol

Reliable Germicide and Preservative

Sterozol is a non-coloring, non-interfering liquid which can be used in any wet operation:

- For inhibiting microbial action on hides and skins in process
- For inhibiting mold on stock and leather in process
- For preserving finishes

Sterozol's low relative toxicity, ease of handling, and economy have contributed in a large measure to its acceptance in the trade.

Sebacol

. . . for dependable unhairing

Sebacol produces clean, uniform, quality leather under varied beamhouse practices.

Biobate

. . . for effective bating

Biobate provides controlled, effective enzymatic action during bating for all types of leather.

WALLERSTEIN COMPANY, INC.

180 MADISON AVENUE • NEW YORK 16, N. Y.

Highest Quality

SODIUM SULPHIDE FLAKES

Our flakes dissolve into a PALE YELLOW SEDIMENT FREE solution, denoting an absence of IRON and other heavy metals. LEATHER MANUFACTURERS are especially pleased with our WATER THIN flakes because these flakes need not be pre-dissolved before using.

MANUFACTURED BY

BARIUM REDUCTION CORPORATION

SOUTH CHARLESTON, WEST VIRGINIA

BORNEO **CUTCH** EXTRACT
(MANGROVE BARK EXTRACT)
SAXE CUTCH CORPORATION
500 FIFTH AVENUE NEW YORK 36, N. Y.

UNIFORM TANNER'S OILS
for Every Type of Leather
MARDEN WILD CORPORATION
SOMERVILLE, MASSACHUSETTS
MARDEN WILD OF CANADA, LTD., HALIFAX, N. S.

STRONGER,
BETTER-LOOKING LEATHER...

. . . In shorter processing time! Leather chemists tell us they achieve this result *consistently* with Sun's Leather-Processing Oils. Reason: these oils mix easily, work fast, lubricate fibers uniformly. There's no surface scum; so rapid, thorough tanning produces light, even-colored leathers —superior in quality, temper and tensile strength. For full details, call your nearest Sun Office . . . or write to Sun Oil Company, Philadelphia 3, Pa. *In Canada:* Sun Oil Company Ltd., Toronto and Montreal.

INDUSTRIAL PRODUCTS DEPARTMENT
SUN OIL COMPANY SUNOCO
PHILA. 3, PA. • SUN OIL COMPANY LTD., TORONTO & MONTREAL

Warner

BELL-MINE LIME

Year-round Uniformity
Dependable Source of Supply

WARNER COMPANY

Bellefonte Division, Bellefonte, Pa.

PITTSBURGH - - - - PHILADELPHIA - - - - NEW YORK

THE OHIO LEATHER CO.

Quality Calf Leather

LUXOR - BLACK JETTA
KAFFORITE - KOZY - JILL JETTA
EMBOSSED CALF - WHITE WASHETTE

TANNERY & GENERAL OFFICES: GIRARD, OHIO
BOSTON • NEW YORK • ST. LOUIS • CHICAGO

EISENDRATH FINE CALF LEATHERS

IN COLORS AND BLACK

B. D. Eisendrath Tanning Company

801 Merchandise Mart, Chicago, Ill. • Tannery at Racine, Wisconsin

92 South St , Boston, Mass., Day Gormley Leather Co. 29 W. 36th St., New York City, Eugene Williams

EST. 1908

MORITE BRAND

Sulphonated and Compounded

OILS

EST. 1908

WHITTEMORE-WRIGHT COMPANY, INC.

62 ALFORD ST. CHARLESTOWN DISTRICT BOSTON, MASS.

PRESTO

The Original Dry Color
for Splits and Suede
(also in paste form)

PRESTO COLOR COMPANY
WEST ALLIS 14, WIS.

Dry Colors ❖ ❖ Finishes

when you want

BORAX AND BORIC ACID HAVE LONG BEEN USED IN THE TANNING AND FINISHING OF GOOD LEATHER

borax or **boric acid**

think first of

SEND TODAY FOR FREE BOOKLET: "PROCESSING HEAVY LEATHER"

PACIFIC COAST BORAX CO.

DIVISION OF BORAX CONSOLIDATED, LIMITED

NEW YORK • LOS ANGELES • CLEVELAND • CHICAGO

Distributors located in principal cities throughout the U.S.

MANUFACTURERS OF FAMOUS "20 MULE TEAM" PACKAGE PRODUCTS

REILLY-WHITEMAN-WALTON CO.

CONSHOHOCKEN, PA.

THE LEATHER MANUFACTURER

ESTABLISHED 1883

Exclusively a Tannery Paper

Devoted to Leather Technology, Tanning and Finishing of Leather, Tannery News and Markets.

Affords complete tannery coverage, concentrated among tanners, chemists and buyers of materials, raw stock and equipment.

Technical articles and newsworthy features invited for publication.

THE LEATHER MANUFACTURER

NEW YORK OFFICE
154 Nassau St.

BOSTON OFFICE
683 Atlantic Ave.

DIRECT ROUTE INTO TANNERIES

Shoe and Leather REPORTER

TANNERY BUYER

THE TECHNICAL JOURNAL FOR SUPERINTENDENTS, CHEMISTS, TANNERS AND BUYERS

The TANNERY BUYER Section of the *Shoe and Leather Reporter* is published the third issue every month and is read by every important executive, superintendent, chemist and buyer.

Tell your message to these men who buy your product in the TANNERY BUYER.

SHOE AND LEATHER REPORTER

Executive Offices: 207 ESSEX STREET, BOSTON 11, MASS.

Representatives in

CHICAGO • LONDON, ENG. • PHILADELPHIA • WASHINGTON
ST. LOUIS • NEW YORK • LOS ANGELES • SAN FRANCISCO

Salem Oil & Grease Co.

FAT LIQUORS

FEATURING

CONTROLLED PENETRATION

●

SALEM, MASSACHUSETTS

STANDARD HIDE POWDER

A material made to specifications and used internationally for the analysis of vegetable tanning materials

FRANK F. MARSHALL
RIDGWAY · PENNSYLVANIA

Garden State Tanning Inc.
Pine Grove, Pa.

Manufacturers of
Upholstery Leather

New York Office **330 Fifth Avenue**

DIAMOND ALKALI CHEMICALS
Fatliquors
For every type of leather
DIAMOND ALKALI CO.
CLEVELAND 14, OHIO

KEPEC FINISHES · KCC CHEMICALS

KEPECO EMULLO FINNALINE KEEPA-SHINE UNI-LAK (Reg. U. S. Pat. Office) KEPOLAC FONDO

KEPEC CHEMICAL CORPORATION
MILWAUKEE 1, WISCONSIN

finest products fastest service

TRASK EST. 1924

TANNING EXTRACTS
SULFONATED OILS
STUFFING GREASES
LIGNOSULFONATES

TELEPHONE *BOulevard 8-2030*

ARTHUR C. TRASK CO.
4103 So. LaSalle St., Chicago 9
CABLE: *Actrask* **TELETYPE:** CG1478

2 to 1

That's the standing of LEATHER AND SHOES in the tanning industry.

The latest circulation statement shows that LEATHER AND SHOES has 108% more paid and audited circulation among tanners (audited by the Audit Bureau of Circulations). That's more than double the number of paid subscribers of any other magazine.

But *readership* is even more important. A recent study revealed that at least 3500 top level executives in the tanning industry are reading LEATHER AND SHOES.

Consider the facts: LEATHER AND SHOES—
. . . does the outstanding job in editorial service.
. . . has twice the paid circulation and considerably more readership.
. . . carries more than double in advertising volume.
. . . does *not* sell advertising on its front cover.
. . . is the industry's most dynamic business paper.

An investment in a subscription to LEATHER AND SHOES will pay dividends in knowledge—an investment in advertising in LEATHER AND SHOES will pay dividends in success. If you want more facts, write us today.

L&S

LEATHER AND SHOES
300 W. ADAMS STREET
CHICAGO 6, ILLINOIS

Finishes
for all types of
Leather

FINE LEATHER FINISHES
NLF

NEWARK
LEATHER FINISH CO.
8 WILHELM ST. HARRISON, N. J.
Telephone: Humboldt 5-3470

HOWES LEATHER CO. INC.
SOLE LEATHER
•
Tanners Cut Sole Division
•
CUT SOLES
BOSTON, MASS.
ST. LOUIS, MO. CHICAGO, ILL.

BONA ALLEN, INC.
Buford, Georgia
TANNERS SINCE 1873
•
Finest English Rein
and Strap Leather
Latigotan Harness Leather
Manufacturers of genuine English type and full rigged hand tooled roping saddles.

1900 **1954**

54 YEARS

SERVING THE LEATHER INDUSTRY

Manufacturers of

- *Vinyl Waterproof Finishes*
- *Highly Concentrated Waterproof Finishes*
- *Glossy Bright Non-flammable Finishes*
- *Low Cost Back Pastes*

A complete line of binders, fillers, water soluble and solvent type top finishes.

APEX
MARK of QUALITY
Established 1900
Apex Chemical Co., Inc.
225 West 34th St., New York 1, N. Y.

UNION TANNERS SUGAR CHIPPED OR BILLETS
UNIFORM CLEAR NON-FOAMING UNIFORM CLEAR
CHIPPED OR BILLETS UNION TANNERS SUGAR
NO NG
UN ETS
UN EAR
CH GAR
NON-FOAMING UNIFORM CLEAR NON-FOAMING
UNION TANNERS SUGAR CHIPPED OR BILLETS
UNIFORM CLEAR NON-FOAMING UNIFORM CLEAR

UNION STARCH & REFINING CO.
Established 1903
General Offices: COLUMBUS, INDIANA

TANIMEX CORP.

350 Fifth Avenue **New York 1, N. Y.**

Prime Importers of

QUEBRACHO EXTRACT

WATTLE EXTRACT H. E. C. BRAND

CHESTNUT EXTRACT LION'S HEAD BRAND

All available in Solid, Pulverized and Spray Dried form.

Raw Tanning Materials of all descriptions.

Always Foremost

Armour's QUALITY Leathers USA

SOLE and UPPER LEATHER

●

ARMOUR LEATHER CO.

Chicago Boston New York

LEATHER
& TANNING MATERIALS
TESTING & RESEARCH
Sampling in all U.S. Ports
PENNIMAN & BROWNE, INC.
CHEMISTS · ENGINEERS · INSPECTORS
341 St. Paul Pl., Balto. 2, Md. MUlberry 5-5811

"The Extension of Knowledge is by the Investigation of Matter".

This space dedicated to
Tanners' Council Research Laboratory
by a Friend

THE TANNERS' COUNCIL
RESEARCH LABORATORY
University of Cincinnati

We serve the Tanning and Leather Industry through a broad program of Research.

RESEARCH
has Two functions
To produce a better Product and to do it More Economically.

THE TANNERS' COUNCIL
RESEARCH LABORATORY
UNIVERSITY OF CINCINNATI

WHEN
YOU
BUY
TANNERS'
CORN SUGARS
CORN SYRUP
CORN STARCH
LACTIC ACID
REMEMBER

CLINTON

CLINTON FOODS INC.
CLINTON, IOWA

Get the full value of full, bloomy undertones

You get the value of deep penetration . . . uniform, level shades . . . excellent exhaustion properties . . . when you rely on Du Pont leather dyes. You also find a wide range of colors and shades to choose from.

Take advantage of the value features offered by the Du Pont leather dyes. Du Pont technicians will be glad to help you select and apply the dyes best suited to your needs. Write to E. I. du Pont de Nemours & Co. (Inc.), Dyes and Chemicals Division, Wilmington 98, Delaware.

DU PONT *Du Pont Dyes*

BETTER THINGS FOR BETTER LIVING . . . THROUGH CHEMISTRY

Some Du Pont Dyes for Garment Leathers

Du Pont Orange RO

Du Pont Resorcin Brown 5G Conc. 200%

"PONTACHROME"* Brown G

Du Pont Chromate Brown EBN

"PONTACYL"* Fast Red AS Extra Conc.

"PONTACYL"* Fast Blue 5R Conc.

*REG. U.S. PAT. OFF.

PROGIL

LION'S HEAD BRANDS

The Hall-Mark of **Chestnut Extract** at its best.

Made in France for a half century from live trees.

Modern equipment in four producing plants.

Continuous research.

Unvarying uniformity of high purity and color.

Ordinary Chestnut and special adjusted pH extracts.

Liquid—Solid—Pulverized—Spray-Dried.

Sole Agent for U.S.A. and Canada

TANIMEX CORPORATION

350 Fifth Avenue **New York 1, N. Y.**

Emergency shipments from U.S.A. Warehouse.

LEATHER and TANNING MATERIALS

CONSULTING • TESTING • RESEARCH • DEVELOPMENT
for the
TANNING AND ALLIED INDUSTRIES

Specialists: Sampling and Testing of Tanning Materials

UNITED STATES TESTING COMPANY

INCORPORATED
1950 Park Avenue, Hoboken, N. J.

FOR VEGETABLE TANNED SOLE LEATHER

THE BEST

BESCO

FOR CHROME CHROME RETAN SOLE LEATHER

COMPOUNDS

TANNERS' SUGAR **LACTIC ACID**

BUFFALO EXTRACT & SUPPLY CO. -:- BUFFALO, N. Y.

1st CHOICE

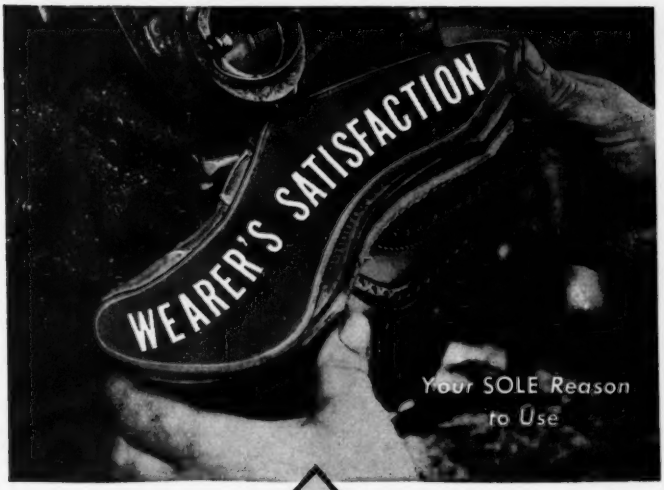
for Higher Quality Leather Production

L.H. LINCOLN & SON, INC. LINCO PRODUCTS COUDERSPORT, PA.

Better Grading Figures!
Better Cutting Figures!
Overall Economy!

Extracts — Pancreatic Bates — Fillers
Sole Leather Finishes - Tanners Sugar
Tanners Lime — Chemicals

L.H. LINCOLN & SON, INC.
COUDERSPORT, PA.



DIAMOND A COMPOUND

TESTED and proved for 40 years—Diamond A is recognized as the Tanners' standard sponging and washing compound.

Here's why. Diamond A does a *double* job — (1) It prepares sole leather for rolling and protects the grain. (2) Used as a dip after rolling, it toughens the grain and improves color and finish.

Why delay? Let the Borne, Scrymser representative give you full particulars on Diamond A. You'll agree it's in a class by itself.

OTHER BORNE, SCRYMSER SPECIALTIES
(Get the Facts about These, Too!)
P COMPOUND for WHEELING
A COMPOUND for SPONGING
Supreme A Compound
Bretolene • Saxon Oil

BORNE SCRYMSER Since 1874
Our Laboratory Facilities are always at your disposal

BORNE, SCRYMSER COMPANY Elizabeth, N. J. Charlotte, N. C.

THE TANNERS' COUNCIL RESEARCH LABORATORY

at

THE UNIVERSITY OF CINCINNATI

is

THE DEPARTMENT OF BASIC SCIENCE

in

THE GRADUATE SCHOOL OF ARTS AND SCIENCE

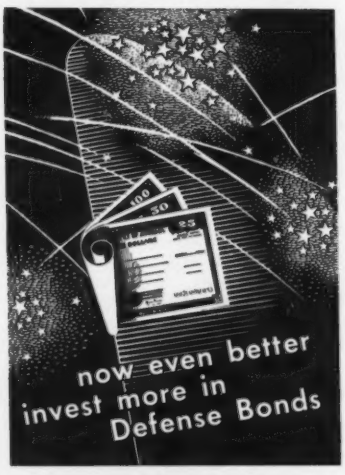
The purpose of the laboratory is to conduct scientific research in the fields of Science concerned with Tanning and Leather.

To train Chemists in the technique of research and prepare them for Industry.

This Laboratory serves as the Official Technical Headquarters for the Tanning Industry of the United States.

Your inquiries will be gladly answered.

Address DR. FRED O'FLAHERTY, Director
Tanners' Council Laboratory
University of Cincinnati
Cincinnati 21, Ohio.



RESEARCH PAYS DIVIDENDS

when Properly Applied.

THE TANNER'S COUNCIL RESEARCH LABORATORY
University of Cincinnati

INDEX TO ADVERTISERS

AMERICAN CYANAMID COMPANY, Leather Chemicals Department V
AMERICAN EXTRACT CO. ..... Outside Back Cover
APEX CHEMICAL CO., INC. XXXIV
ARKANSAS COMPANY, INC. VI
ARMOUR LEATHER CO. XXXV
ARTHUR C. TRASK CO. XXXI
ARTHUR THOMAS CO. XXII
ATLAS REFINERY XVI
BARIUM REDUCTION CORPORATION XXV
BARKEY IMPORTING CO., INC. ..... VII—XIX
BONA ALLEN, INC. XXXIII
BORNE, SCRYMSER COMPANY XLI
BUCKMAN LABORATORIES, INC. XVII
BUFFALO EXTRACT & SUPPLY CO. XXXIX
CHEMTAN COMPANY XXI
CLINTON FOODS, INC. XXXVI
DIAMOND ALKALI CO. XXXI
E. I. DuPONT DeNEMOURS & CO. XXXVII
EISENDRATH TANNING CO. XXVII
FRANK F. MARSHALL XXXI
GARDEN STATE TANNING INC. XXXI
GENERAL DYESTUFF COMPANY ..... VIII—IX
HOOKER ELECTROCHEMICAL CO. XVIII
HOWES LEATHER CO., INC. XXXIII
INTERNATIONAL PRODUCTS CORP. XII
KEPEC CHEMICAL CORPORATION XXXI
LEATHER AND SHOES XXXII
LEATHER MANUFACTURER, THE XXIX
L. H. LINCOLN & SON, INC. XL
MARDEN WILD CORPORATION XXVI
MEAD CORPORATION, THE XIII
NEWARK LEATHER FINISH CO. XXXIII
NOPCO CHEMICAL CO. XXIII
OHIO LEATHER CO., THE XXVII
OLSON SALES AGENCY, THE ..... Inside Front Cover
PACIFIC COAST BORAX CO. XXVIII
PENNIMAN & BROWNE, INC. XXXVI
PRESTO COLOR CO. XXVIII
REILLY-WHITEMAN-WALTON CO XXIX
RIVER PLATE CORPORATION, THE XIV
ROBESON PROCESS CO. II
ROHM & HAAS IV
SALEM OIL & GREASE CO. XXX
SAXE CUTCH CORPORATION XXVI
SHOE & LEATHER REPORTER XXX
SOCONY-VACUUM OIL CO. I
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL & DYE CORP. XI
SOUTH AFRICAN WATTLE EXTRACT MFRS. ASSO. XV
SUN OIL COMPANY XXVI
TANEXCO, INC. ..... XLIV—Inside Back Cover
TANIMEX CORPORATION ..... XXXV—XXXVIII
TANNERS' COUNCIL RESEARCH LABORATORY ..... XXXVI—XLII
TEAS EXTRACT CO. III
UNION STARCH & REFINING CO. XXXIV
UNITED STATES TESTNG COMPANY XXXIX
WALLERSTEIN COMPANY, INC. XXIV
WARNER CO. XXVII
WHITTEMORE-WRIGHT CO. XXVIII
WOLF, JACQUES & CO. X
YOUNG CO., J. S. XX

ITALIAN

CHESTNUT EXTRACT

Solid — Powder — Spray Dried

also

MELLOWED CHESTNUT

Highly Soluble — Weight Giving — Good Color

MADE FROM LIVE WOOD

TYPICAL A.L.C.A. ANALYSIS

	Solid	Mellowed Powder	Spray Dried
TANNIN	61.72	65.95	73.5
NON-TANNIN	21.65	26.67	19.1
INSOLUBLES	.65	.67	.7
WATER	15.98	6.71	6.7

STAINLESS SUMAC CRYSTALS

HIGHEST QUALITY—MADE UNDER THE SUPERVISION OF THE WORLD'S LEADING EXTRACT CHEMISTS

SOLE AGENTS

TANEXCO, INC.

549 W. Washington Blvd. Chicago, Illinois

MYRTAN

A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

TANNIN	61.55
NON-TANNIN	16.03
INSOLUBLES	1.70
WATER	20.72

Also Available as Liquid with 30% Tannin

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

For further information address:

TANEXCO, INC.

349 WEST WASHINGTON BLVD., CHICAGO 6, ILLINOIS

SOLE AGENTS
U. S. A.

DERMABATE
COMPOUNDS
LIQUID EXTRACTS

HEMLOCK
OAK
MANGROVE
WATTLE
STAINLESS SUMAC
ORDINARY SUMAC
QUEBRACHO
SPECIAL DIPPING EXTRACTS
RAPID TAN "G"

★

AMERICAN EXTRACT CO.

Manufacturers of the Largest
Variety of Vegetable Tanning Extracts
Established 1887

PORT ALLEGANY, PA.

CANADIAN REPRESENTATIVES:
McArthur Chemical Co., Ltd., 20 St. Paul St., West, Montreal; 73 King St., West Toronto

ENGLISH REPRESENTATIVES:
Roy Wilson, Dickson, Ltd., 7-8 Railway Approach, London, S. E. 1